Inorganic Chemistry

PART II

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PREFACE.

THE present volume (Part II.) contains the subject-matter which, in our opinion, is suitable for those who, having mastered Part I., intend to devote at least two years more to the study of inorganic chemistry, while at the same time working at organic chemistry and other subjects, with the view of obtaining a university pass-degree.

It has been our aim throughout to present the fundamental principles and theories of the science, rather than a mere collection of facts, and thus to afford a sound basis from which the student may proceed to specialise in one or other of the branches of chemistry.

With this purpose in view, we have devoted the earlier portion of Part II. to a further consideration of physical and chemical change, to a study of chemical equilibrium, the determination of molecular weight, and the ionic dissociation theory, in the hope that when the student subsequently considers the description of the elements and their compounds, he will do so in the light of the general principles to which he has been introduced.

The rest of Part II. consists of a systematic account of the better-known elements, a chapter on the periodic system, and short references to spectrum analysis and radio-activity. In arranging this subject-matter we have been guided more particularly by our experience that the order in which the elements are described in a text-book should be one which is also suitable for the lecture-room, and that, for this reason, it is inadvisable to deal with all the non-metals before describing some of the metals. A long, uninterrupted course of lectures on the metals is apt to become wearisome to the student after the 'fireworks' which enliven a course on the non-metals; moreover, a knowledge of some of the compounds of the metals is desirable at an early stage of the second-year course, owing to the necessary and frequent use of these compounds in the laboratory.

Those portions of the text which may be omitted during the second-year course, and which contain the subject-matter of the third-year course, are distinguished by a marginal line. While recognising the difficulty of attempting any such distinction, owing to the great diversity of opinion which may be held as to what should be included in each of these courses, we believe that some clear demarcation in a text-book is highly desirable, if not essential; and the plan adopted here, while enabling the student to select what he requires, does not suffer from the many disadvantages which would attend a complete separation of the subject-matter into two successive parts.

We are indebted to Dr A. Lapworth, F.R.S., for certain sections of the text relating to physical chemistry, and also for assistance in reading the proof-sheets.

1925

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INORGANIC CHEMISTRY.

PART II.

CHAPTER XXXIV.

Equilibrium between Solids and Liquids.

As progress is made in the study of chemistry it will be seen more and more clearly that it is practically impossible to draw a sharp distinction between physical and chemical changes. For this reason, although changes in state have been classed together as physical changes (p. 40), and an attempt to define chemical change has been made (p. 182), attention has also been drawn to two important qualifying considerations: (*a*) that it is very difficult to say in which class some of the phenomena of solution should be placed (p. 41); and (*b*) that since many chemical changes are easily reversible (p. 86), reversibility is not a distinctive characteristic of physical change.

In spite of the difficulties here indicated, it is convenient to retain the use of the terms 'physical' and 'chemical,' in the senses in which they have already been employed, to distinguish broadly between certain sets of phenomena.

The first subject which may now be considered more fully is rather of a physical than of a chemical character, and concerns the behaviour of solutions. A solution is said to be saturated with a substance when, being in contact with that substance, it retains its composition unchanged so long as the temperature and pressure do not vary. The fact that a saturated solution does not alter in composition is probably due, not to the *cessation* of all change, but to the results of two opposed processes; on the one hand the soluble substance is being dissolved, but on the other hand it is being deposited again, and in any given time just as much substance passes into as passes out of solution.

A system (p. 57) such as a saturated solution, which thus retains a constant composition under constant conditions owing to the occurrence of two opposed changes, is said to be in a *condition* or *state of equilibrium.* The solubility curves already given (p. 25) show, therefore, in each case, the composition of a solution in equilibrium with the solid under the given conditions of temperature and pressure.

Heat of Solution.—In the case of some salts, such as potassium nitrate, the solubility in water *increases* very considerably as the temperature rises; but in the case of others, such as sodium chloride, it increases very little. On the other hand, many salts and other soluble substances show a behaviour very different from that of potassium nitrate or of sodium chloride, inasmuch as the solubility *decreases* as the temperature rises; thus a saturated solution of calcium hydroxide, or of gypsum (p. 226), prepared in the cold, becomes turbid when heated, owing to the separation of some of the dissolved solid. The solubility curves of such substances, therefore, instead of sloping upwards, as do those already given, slope downwards.

Now when any substance passes into solution there is a development or an absorption of heat, which may be considerable, or which may be almost inappreciable. The maximum heat development or absorption (expressed in calories, p. 135), obtainable by dissolving one *gram-molecule* (p. 197) of a substance in an unlimited quantity of water, is termed the **heat of solution** of that substance in water.

The heat of solution of sodium nitrate or potassium nitrate in water is strongly negative, and the cooling effect is quite sensible to the hand when either of these salts is being dissolved. The heat of solution of sodium chloride is also negative, but is only small, so that on adding this salt to water the fall in temperature is not observed unless a thermometer is used. On the other hand, those substances which, like calcium hydroxide and gypsum, decrease in solubility with rise in temperature, have a positive heat of solution.

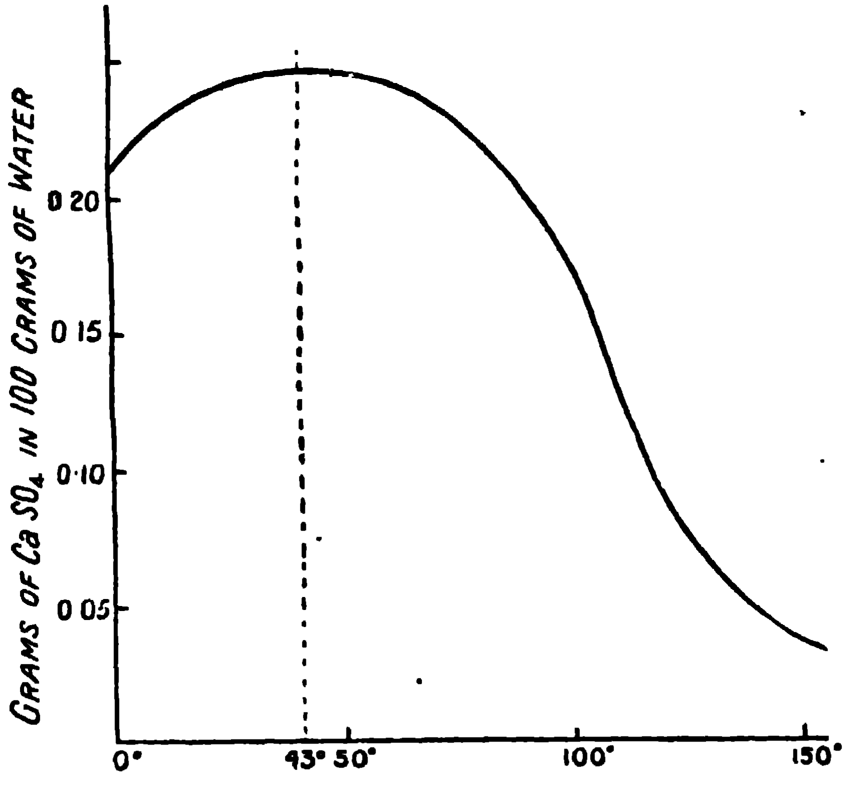

Fig. 80.

This suggested connection between the variation of solubility with temperature and the heat of formation of the saturated solution of the salt holds universally true, and it may be anticipated that if a salt does not change in solubility as the temperature alters, then it dissolves without production either of heat or of cold. In the case of a salt having the solubility curve given in the diagram (fig. 80), it may be inferred that from 0° to 43° the salt dissolves with absorption of heat, but above 43° with production of heat; the highest point on the curve is the point where the heat of solution is 0 and changes from a negative to a positive value, the change being quite gradual throughout. Such is the case with gypsum, $CaSO_4, 2H_2O$.

Many salts take up different proportions of water of hydration at different temperatures (footnote, p. 274), and it is but a short step to the conclusion that if several hydrates of the same salt exist, and these have different heats of solution (as is usually the case), they will also have different types of solubility curves, because each must change in solubility with temperature, in a different manner.

No better example than sodium sulphate can be selected to illustrate what is actually observed in such cases. This salt is easily obtained in two different forms. One of these is the anhydrous salt, Na_2SO_4; the other the hydrated form, $Na_2SO_4, 10H_2O$ (p. 226), as it exists in Glauber's salt, from which the first is easily obtained by dehydration (p. 38).

The hydrated form dissolves in water at ordinary temperatures with absorption of heat, and consequently increases in solubility as the temperature rises. The anhydrous form, on the other hand, can hardly be said to form a saturated solution in water at ordinary temperatures, because when brought into contact with cold water it becomes converted into the hydrated form. Above 33°, however, the anhydrous salt does not undergo this change, and dissolves with evolution of heat; hence above this temperature its solubility curve slopes in the opposite direction to that of the curve of the hydrated salt.

The quantities of dissolved Na_2SO_4 in saturated solutions prepared from the two forms of the salt have been determined, and it has been found that the two solubility curves are really continuous and meet at the temperature 33°, as shown in fig. 81. The line *AO* gives the solubility (in grams of Na_2SO_4 per 100 grams of water) of the hydrated salt, and *OD* that of the anhydrous salt. *O*, the point at which the curves meet, corresponds with 33°, and a concentration of about 50 grams of Na_2SO_4 per 100 of water.

It is evident that at 33° (the point *O*) the saturated solutions of both forms have the same concentration, and therefore the solution and *both* solid forms of the salt can exist together in a state of equilibrium; at no other temperature is this possible. Above 33° the saturated solution prepared from crystals of Na_2SO_4, $10H_2O$ contains more Na_2SO_4 than a saturated solution prepared from the anhydrous salt, and would therefore (if given the opportunity) deposit the latter form. Below 33° the inverse holds good, and a saturated solution of the anhydrous salt deposits the hydrated solid. In either case the change continues until the condition of equilibrium indicated by the curve *AOD* is attained.

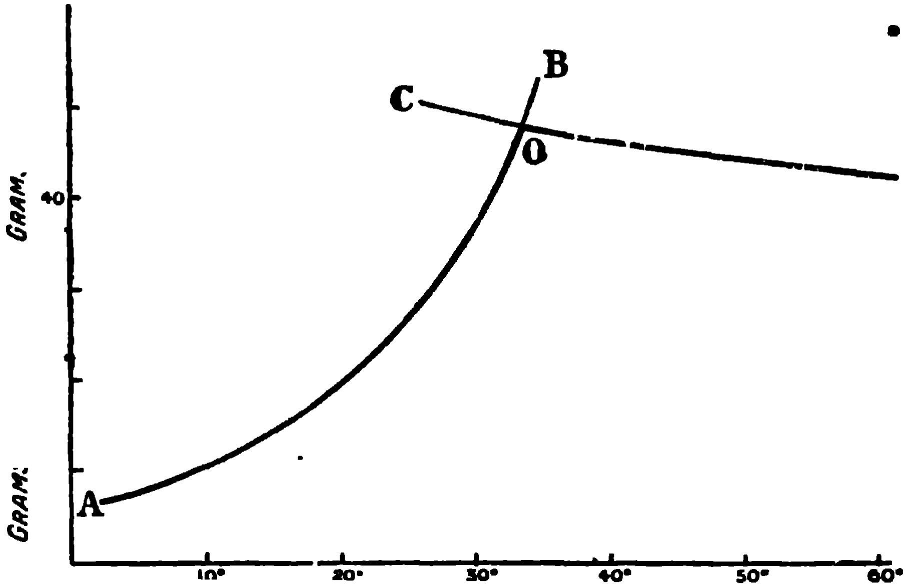

Fig. 81.

Two conclusions may be emphasised. (1) At 33° crystals of Na_2SO_4, $10H_2O$, in presence of a trace of liquid moisture, will usually appear to dissolve in its water of crystallisation (p. 38), forming a saturated solution of both Na_2SO_4 and Na_2SO_4, $10H_2O$; on raising the temperature slightly above

33°, this liquid will deposit increasing quantities of Na_2SO_4. (2) When attempts are made to trace the solubility curve of either $Na_2SO_4, 10H_2O$ or Na_2SO_4, taking those precautions which are necessary in order to obtain supersaturated solutions (see below), then the curves will continue beyond *O*, as shown by the lines *OB*, *OC* in the diagram.

At one time it was generally believed that solubility curves of the above type indicated that the salt hydrates existed in the solutions, as such, and decomposed in the solution at the temperature of the *break*. It is evident from what has been said that the break is the point where the solubility curves of the two different solid modifications cross one another. Its existence in an experimental solubility curve merely supplies evidence of the existence of two such solids, and has no direct bearing on the state of the salts in the solution.

SUPERSATURATED SOLUTIONS.

When a *saturated* solution of $Na_2SO_4, 10H_2O$, prepared say at 30°, is poured into a warm, clean flask (taking care that the solution is free from any suspended crystals), and the neck of the flask is then plugged with cotton-wool to prevent the entrance of dust,* the solution may afterwards be cooled, say to 15°, without any crystalline deposit whatsoever being formed. If now the smallest particle of a crystal of $Na_2SO_4, 10H_2O$ is dropped into the solution (a process often called 'seeding'), crystallisation immediately sets in (accompanied by a rise in temperature), and continues until the condition of equilibrium shown by the solubility curve is attained.

A solution which shows this behaviour is said to be **supersaturated.** So long as it is *not* in contact with a crystal of $Na_2SO_4, 10H_2O$ it is *stable*, and may be kept indefinitely without change in composition; but in contact with such a crystal it is *unstable*. For this reason the supersaturated solution (which is not in the *most* stable condition) is said to be in a *metastable* condition.

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* Atmospheric dust may contain crystals of $Na_2SO_4, 10H_2O$, and must therefore be excluded, otherwise it may be impossible to prepare a supersaturated solution.

Supersaturated solutions of many other solids may be prepared (p. 497), and in carrying out solubility determinations care must be taken that the solutions examined are not supersaturated.

In a similar manner many pure liquids may be cooled below their melting- (freezing) points, or heated above their boiling-points, without a change in state taking place, provided that clean vessels are employed and dust is carefully excluded. Liquids in this metastable condition are said to be *supercooled* or *superheated*, as the case may be. Below certain temperatures supercooled liquids and supersaturated solutions deposit crystals spontaneously (i.e. without being 'seeded'), the *metastable* having passed into an *instable* condition.

CRYOHYDRATES.

When a *saturated* solution of common salt is cooled slowly, crystals of pure *salt* separate and the solution becomes less concentrated; on its continuing to cool, a further quantity of pure salt is deposited, and this separation may be continued below the freezing-point of water without any ice being formed; the composition of the remaining liquid depends, therefore, on the temperature. When, on the other hand, a very *dilute* solution of salt is cooled slowly, it begins to deposit crystals of pure *ice* below 0°, the exact temperature depending on the concentration of the solution. As this deposition proceeds and the temperature continues to fall, the solution becomes more and more concentrated, but, as in the former case, the final composition of the liquid simply depends on the temperature.

In the diagram (fig. 82), *A* represents the freezing-point (0°) of an infinitely dilute solution of salt, and the line *AB* shows the temperature at which ice is deposited as the solution becomes stronger. The line *CD* shows the temperature at which salt is deposited from saturated solutions.

During these cooling processes, therefore, the saturated solution and the dilute solution are approaching one another in composition more and more closely as the temperature falls, and provided that the separation of salt or of ice, as the case may be, continues regularly, the compositions of the two liquids finally become identical at the point *O*. In other words, if a start is made with a strong or with a weak solution, there is ultimately obtained a liquid which on further cooling may deposit either salt or ice. If the former were to separate the solution would become more dilute, and would have the composition of one which formerly deposited ice; if the latter, then the solution would become more concentrated, and would have the composition of one which formerly deposited salt. Hence, unless the conditions are such that supersaturated solutions can exist at the point where the compositions of the two liquids become identical, further withdrawal of heat will cause *both* salt *and* ice to separate simultaneously. Now if the proportion by weight of salt to ice in the deposit is greater (or less) than in the solution, then the solution would become less (or more) concentrated, and would have the composition of a liquid which had previously deposited ice (or salt) at a higher temperature.

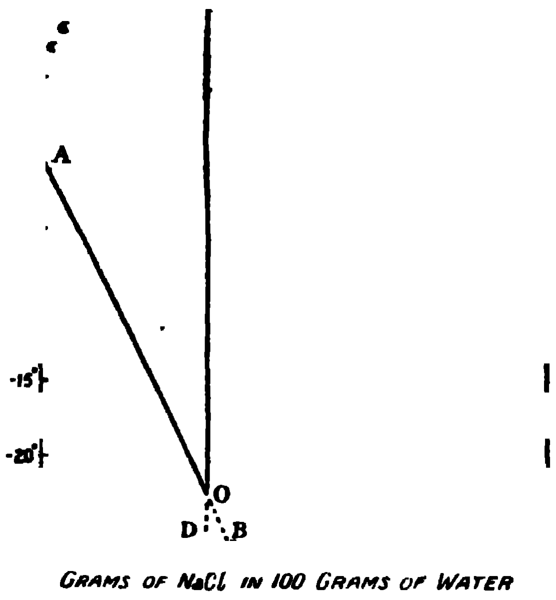

Fig. 82.

Consequently the further abstraction of heat **does not alter** the composition of the liquid; the solution still remains saturated with salt, and, in a sense, with ice, and gradually solidifies completely without any further fall in temperature.

Here, then, is a case of the freezing of a *mixture* without change of temperature or composition, so that the properties of a compound are simulated.

Solid mixtures so formed and having these properties were at one time thought to be definite hydrates and were termed **cryohydrates.** To the naked eye, however, cryohydrates present the appearance of an opaque mass without definite crystalline habit (p. 319), and under the microscope they are seen to contain two kinds of crystals; their physical properties, too, such as heat of solution and density, are the mean of those of their component solid materials, which is not the rule with chemical compounds. For these reasons cryohydrates are no longer regarded as definite hydrates.

On the temperature at which such cryohydrates separate depends the degree of cold attainable by freezing mixtures of ice and salts (p. 8). When salt is added to moist ice it dissolves, forming a solution which is no longer in equilibrium with the ice at 0°; the latter melts, absorbing heat, and this process goes on, if the mixture is suitably protected from external warmth, until the solution has the temperature and concentration which corresponds to the cryohydrate point. It is then saturated both to ice and to salt, and consequently no further change occurs.

Cryohydrates of many substances may be obtained; moreover, liquids which solidify without change in composition or temperature may be produced from innumerable pairs of substances. The solid mixture thus formed melts at a constant temperature and is known as a **eutectic**; a cryohydrate is only one particular kind of eutectic in which ice is one of the solids present.

Alloys, the products obtained when fused mixtures of metals are allowed to cool, frequently consist to a great extent of such eutectics embedded in varying amounts of other solids, which may consist of some of the pure component metals of the alloy, or of compounds of these components. Thus a liquid mixture of copper and silver, when cooled, deposits first either pure crystals of copper or of silver, according to the proportions of the metals present. The molten mass continues to change in composition until it consists of 40 atomic proportions of copper to 60 atomic proportions of silver, at which point it solidifies at a constant temperature (778°) without change in composition.

* A eutectic shares with a compound the property of fusing at a constant temperature and without change of composition, but may be distinguished from a compound by means similar to those applied to discriminate between cryohydrates and true salt hydrates. The simplest method of distinguishing between such constant melting mixtures and chemical individuals depends on the fact that when the composition of a liquid eutectic is varied by the addition of any of its components it begins to freeze at a *higher* temperature than the eutectic does, while in the case of a compound of the same substances the addition of any of the constituents would cause a *depression* of the freezing-point.

By a careful examination of the freezing-point of mixtures of metals or of other substances miscible in the liquid state in varying proportions, it is thus possible to determine whether they yield compounds, or eutectics, or both.

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* ***A considerable proportion of the matter contained in this volume is not required by students who are working for second year or intermediate examinations such as those of most universities or of the Board of Education (Stage II.). These parts of the text are marked with a line, so that their study may be postponed until the student enters on the third year course.***

CHAPTER XXXV.

Crystals—Double Salts—Isomorphism.

The anhydrous or hydrated solids which are deposited from their saturated solutions are generally obtained in the form of *crystals* (p. 31). Normal crystals are homogeneous bodies, the composition being the same in every part, as is also the density. They are bounded by flat planes or faces which, when they intersect, do so in straight lines. Every face on a normal crystal, therefore, is a polygon bounded by straight lines. If a point be taken on any crystal edge and lines be drawn on the two intersecting faces at right angles to the edge, the two lines are inclined to one another at a definite angle which gives the angle between the two faces or the *interfacial angle.*

As a rule, the crystals of any one substance which are deposited under similar conditions bear a marked resemblance to one another; every, or nearly every, face has its representative on all the crystals, and corresponding faces on different crystals may often be identified by mere inspection. The first fundamental **law of crystallography** is that '*the interfacial angle between corresponding faces on different crystals of the same substance is constant, if measured at a fixed temperature, and is independent of the size or development of the faces.*'

This law, however, is only approximately true, for if two crystals are compared, variations of half a degree or even more are sometimes observed, even with good crystals. Nevertheless the *mean* of a sufficiently large number of examples is a constant for any given crystalline modification of a pure substance.

The enormous majority of perfectly developed crystals exhibit some type of symmetry.

The lowest type is *point symmetry*, or that about a point in the crystal, namely, the centre. In this instance, for each face on the crystal there is another, parallel to it on the other side of the centre.

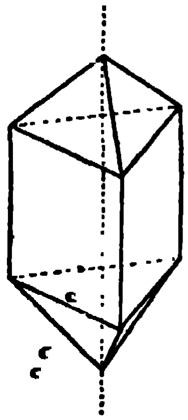
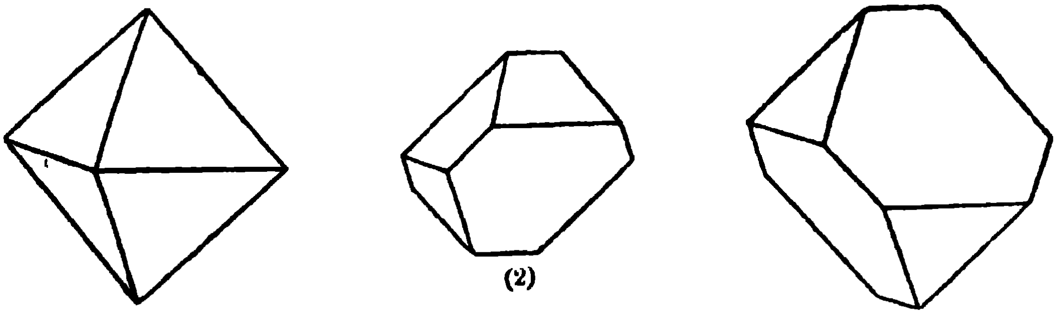


Fig. 83.

A crystal has a *plane of symmetry* when a plane may be drawn through the mass of the crystal in such a direction that the faces lie in pairs symmetrically disposed with regard to this plane; with a perfectly developed crystal the plane cuts it into two parts related to one another as an object and its reflection in this plane.

A crystal has an *axis of symmetry* when it may be rotated about some line (passing through the centre of the crystal) through some submultiple of 360°, so that each face will occupy the position previously taken by another. That is, the crystal may be cut by several planes, meeting at the axis, into portions each of which corresponds exactly with the others; with a perfectly developed crystal the various sections will be exactly similar in all respects.



(1) (2) (3)

Fig. 84.

A perfectly developed crystal of this kind, set in a mould, if taken out and twisted through some submultiple of 360°, would once more fit the mould exactly in a new position.

The crystal shown in fig. 83, for example, may be so twisted through $\frac{360^\circ}{3}$; this crystal, therefore, has an axis of 3-fold symmetry.

Only axes of 2, 3, 4, and 6-fold symmetry are possible by the laws of crystallography.

A *perfectly developed crystal* is one in which corresponding faces all lie at an equal distance from the centre. Such a crystal is rarely, if ever, met with in practice, as growth usually occurs more quickly in some directions than in others. A perfectly developed octahedron, for example, has the form (1), fig 84, but instead of this form, others, such as (2) or (3), are often produced owing to special development of certain faces.

Similarly, in the place of the perfectly developed crystal (4), fig. 85, forms such as (5) and (6) may be obtained.

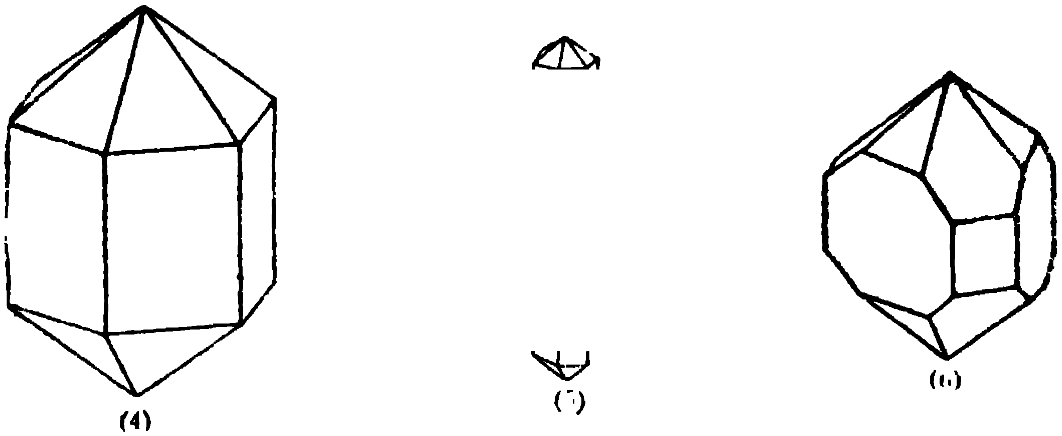

(4) (5) (6)

Fig. 85.

When crystals differ from one another in the manner illustrated by each of these two cases, they are said to have different *habits*.

Let XOX', YOY', and ZOZ' (fig 86) be three imaginary straight lines (crystallographic axes) parallel to any three possible edges of the crystal, and let these be cut by the plane of one of the crystal faces at the points x, y, and z respectively. The lines xy, yz, and xz represent the lines of intersection of the plane of the crystal face with the co ordinate planes of the crystal.

The second fundamental **law of crystallography** states that '*if the relative lengths* ox, oy, *and* oz *are represented by* $a : b : c$, *then the corresponding values for* ox', oy', *and* oz' *for any other face on the crystal will be represented by the numbers* $pa : qb : rc$, *where* p, q, *and r are small whole numbers'* (including zero). If the face cuts any axis on the opposite side to O from that indicated, that is, on the side X', Y', or Z', then the corresponding multiplier p, q, or r is negative in sign.

In Miller's system of crystallographic nomenclature, which is the one now most generally adopted in chemical crystallography, the numbers $\frac{a}{b} : 1 : \frac{c}{b}$, selected a rule from the typical faces, are known as the *axial ratios* of the crystal.

Any face on the crystal is determined by the multipliers p, q, and r, but whole numbers proportional to the reciprocals $\frac{1}{p}$, $\frac{1}{q}$, and $\frac{1}{r}$ are used in this system, and are known as the '*indices*' of the face. Thus if the multipliers of a face are 2, 3, and 4 respectively, its *indices* are the smallest whole numbers proportional to ½, ⅓, and ¼, that is, 6, 4, and 3, and the formula of the face is 643.

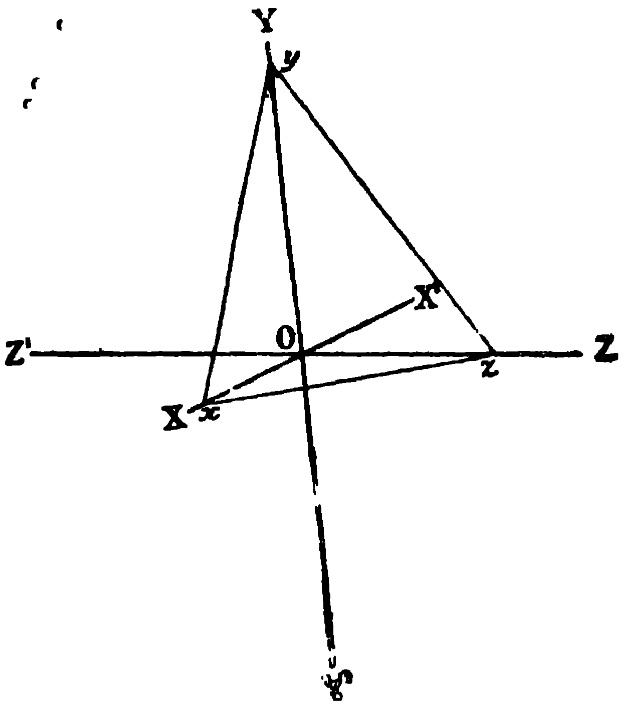


Fig. 86.

If some of the multipliers of a face are negative in sign, this is indicated by a line drawn above the indices thus: $6\bar{4}3$. The formula of a parallel face on the opposite side of the centre is obtained in all cases by a total inversion of the positive and negative signs. Thus $6\bar{4}\bar{3}$ and $\bar{6}48$ represent parallel faces.

Owing to the circumstance that crystals almost invariably contain planes, axes, or points of symmetry, it is seldom, if ever, that one face occurs without at least one other corresponding to it. Thus all the faces of the regular octahedron may be regarded as corresponding to one another as the result of the type of symmetry inherent to the crystal, and such related faces are said to make up a 'form.' A 'form' is indicated by enclosing the formula of one of its component faces in brackets, thus $\{643\}$.

The cube is made up of faces, each of which cuts one axis only, and the others at an infinite distance. Thus one face cutting only the X axis and on the right of the centre has the multipliers 1, ∞, ∞, and this face is therefore rendered as $1 \frac{1}{\infty} \frac{1}{\infty}$ or 100. The cube is therefore {100}, while the faces of which it is composed are 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$. The regular octahedron is {111}, and its component faces 111, $\bar{1}\bar{1}\bar{1}$, $\bar{1}11$, $1\bar{1}\bar{1}$, $1\bar{1}1$, $\bar{1}1\bar{1}$, $11\bar{1}$, $\bar{1}\bar{1}1$.

As a rule crystals are combinations of forms; thus the one shown (fig. 87) is a combination of the cube and octahedron, and is often found in crystals of alum.

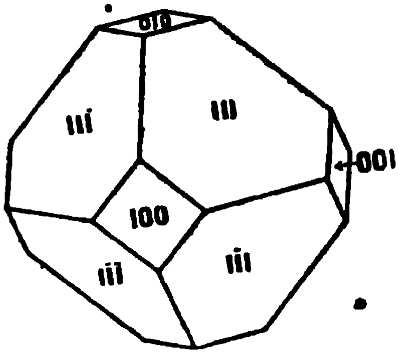


Fig. 87.

Crystals are divided into various systems, but the broadest mode of classification is as follows:

(1) *The Cubic System.*—Includes crystals with three equal axes all at right angles to one another. *Examples.*—The regular cube: common salt, potassium chloride, fluor-spar. Octahedron: alums. Other forms: iron pyrites, barium nitrate.

(2) *The Hexagonal System.*—One axis of threefold or sixfold symmetry. For convenience this system is represented as having three crystallographic axes of equal length in one plane and equally inclined to one another, and a fourth (the axis of symmetry) at right angles to the plane of the other three, and of different length from the others (fig. 88). *Examples.*—Calc-spar, ice, quartz, sodium nitrate.

Fig. 88.

(3) *The Tetragonal System.*—Three axes at right angles, two of equal length, the third of different length. *Examples*—Tin stone, boron.

(4) *The Orthorhombic System.*—Three axes at right angles, of unequal lengths (a very common type). *Examples.*—Rhombic sulphur, iodine, nitre.

(5) *The Monoclinic (or Monosymmetric) System.*—Two axes not at right angles to one another, and a third at right angles to the plane of the first two. The three axes of different lengths. *Examples.*—Prismatic sulphur, potassium chlorate, Glauber's salt, gypsum, green vitriol.

(6) *The Asymmetric System.*—Three axes of unequal lengths, no two at right angles to one another. *Examples.*—Blue vitriol, potassium dichromate.

As already stated (p. 214), many substances may form crystals of two or more different kinds, usually belonging to different systems. Such substances are termed di-, tri-, or poly-morphous, as the case may be.

Double Salts.

When a solution which contains two salts, or other dissolved solid substances, is concentrated or cooled, the first deposit consists, as a rule, of *one* substance only (p. 32); later, both the dissolved substances may separate side by side, giving a heterogeneous deposit in which the proportions of the substances vary according to the conditions and are not in any definite molecular ratio. In some cases, however, a solution of two substances deposits homogeneous crystals which contain *both* substances in definite and simple *molecular proportions*. When this occurs the proportions of the two substances in the solution may often be varied very considerably without altering the composition of the crystals which are first obtained. Crystals of potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ (p. 295), for example, are deposited from a saturated solution containing potassium sulphate and aluminium sulphate, and, within certain limits, the proportion in which the salts are present in the solution makes no difference as regards the composition of the earlier 'crops' of crystals.

Crystalline substances of this kind are termed **double salts** (p. 295). Many other examples of such double salts will be given later.

An aqueous solution of a double salt shows all the reactions of both the component salts, and the physical and chemical properties of the solution are almost exactly the *mean* of those of solutions of these components. Moreover, there is no evidence that the molecules of either of the components are different in the double salt from what they are in the separate substances, and it would seem that one of the salts merely plays a part analogous to that played by water in a hydrated crystal.

SOLID SOLUTIONS.

Solutions containing two substances may show a behaviour altogether different from that of either of the two types so far referred to. They may give physically homogeneous crystals, the composition of which may *vary* to a greater or less extent. When, for example, a solution containing copper sulphate and ferrous sulphate is allowed to evaporate slowly, and the crystals which are deposited are picked out from time to time and analysed, it is found that each crystal may contain *both* sulphates, but not always in the same proportion.

Again, crystals of dolomite (p. 75) contain both carbonate of calcium and carbonate of magnesium, but probably no two crystals have exactly the same composition. The crystals which separate from a fused mixture of gold and silver contain both these elements, and may contain any proportions whatever of the two components. Silver and zinc also yield crystals containing both metals, but the proportion is only variable within certain limits.

Solids such as these crystals resemble solutions inasmuch as they are homogeneous materials which can vary in composition within limits which are sometimes fixed and sometimes indefinite. For this reason, mixtures of this nature have received the title of '**solid solutions**.'

The behaviour of a liquid mixture which may deposit a solid solution is very different from that of a liquid which deposits only pure crystals of one or more kinds. If a substance is added in small quantity to another with which it may form solid solutions, then the melting or freezing point may actually be raised instead of lowered, according as the mixed crystals which separate contain more or less of the added substance than the liquid does; this is the case, for instance, when silver is added to molten zinc. In the study of alloys, the formation of solid solutions plays a part of the greatest importance. Steels and brass, for example, consist very largely, and perhaps sometimes wholly, of solid solutions of the components.

ISOMORPHISM.

Substances which form solid solutions with one another nearly always belong to the same crystalline system, and the crystalline forms of the separate substances resemble one another very closely. A crystal of the one substance placed in a saturated solution of the other increases in size without any alteration of importance taking place in the magnitude of the interfacial angles. Thus a violet octahedral crystal of chrome alum (p. 510), placed in a saturated solution of potash alum, continues to grow without alteration in crystalline form, and is slowly converted into a much larger octahedral crystal by the deposition of colourless potash alum; further, a supersaturated solution (p. 312) of potash alum immediately crystallises when 'seeded' with a crystal of chrome alum, and *vice versâ.*

Substances which show the above relationship are called **isomorphous**. Other examples of isomorphous substances are the carbonates of calcium and magnesium, gold and silver, the chlorides of potassium and ammonium.

As a rule there is a very close connection between crystalline form and molecular structure; compounds of the same *type* are frequently isomorphous, as will be shown by numerous examples mentioned later (pp. 456, 502, 520, 616).

This fact was discovered by Mitscherlich (in 1819), and in the past it has been made use of for the determination of atomic weights. Since *the crystalline form of compounds of analogous chemical composition is the same* (**the law of Mitscherlich**), if two compounds are known to be isomorphous, and one of them contains an element of unknown atomic weight, this unknown atomic weight may be calculated from the results of analyses.

Example.—Potassium selenate is found to be isomorphous with potassium sulphate. The formula of potassium sulphate is known to be K_2SO_4, and its percentage composition is $K=44{\cdot}8$, $O=36{\cdot}8$, and $S=18{\cdot}4$. An analysis of potassium selenate shows that it contains 35·3 per cent. of potassium; if, therefore, the selenate and the sulphate are of the same type, the percentage of oxygen in the selenate is $\frac{35{\cdot}3 \times 36{\cdot}8}{44{\cdot}8}=29$, and the percentage of *selenium*, by difference, is 35·7.

Now in potassium sulphate 2 gram-atoms (78 g.) of potassium are united with 1 gram-atom (32 g.) of sulphur, and in potassium selenate 78 g. of potassium are united with $\frac{78 \times 35{\cdot}7}{35{\cdot}3}=79$ grams of selenium; hence the atomic weight of selenium is 79.

Certain substances show *isodimorphism*, or even *isopolymorphism*. Thus the sulphates of copper and of iron may be obtained in isomorphous asymmetric crystals having the composition $CuSO_4$, $5H_2O$, and $FeSO_4$, $5H_2O$ respectively, and also in isomorphous monoclinic crystals having the composition $CuSO_4$, $7H_2O$, and $FeSO_4$, $7H_2O$ respectively. This is the reason why these two salts, which usually crystallise in *different* systems, give rise to solid solutions when they are crystallised together.

DIALYSIS, PSEUDO-SOLUTIONS, AND COLLOIDS.

When excess of a dilute solution of hydrochloric acid is treated with a dilute aqueous solution of sodium (meta)silicate no precipitate is produced, although metasilicic acid (p. 293) is probably formed in accordance with the equation,

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl.$$

If the solution is boiled metasilicic acid is precipitated, but at ordinary temperatures no precipitate forms even in the course of some days: it would seem, therefore, that metasilicic acid exists in two forms, one of which is insoluble, the other soluble, in water.

Now it was found by Graham that most substances which are soluble in water can pass through parchment-paper and certain other membranes, whereas some of them do not show this property. If, for example, a dilute solution of sodium chloride or of hydrogen chloride is placed in a **U**-tube made of parchment-paper (free from holes), and this tube is suspended in a vessel of distilled water, as shown in the diagram (fig. 89), the sodium chloride or the hydrogen chloride, as the case may be, rapidly passes or diffuses through the membrane and may be detected in the surrounding water. If, on the other hand, an aqueous solution of glue or gelatine is placed in the **U**-tube, the glue or gelatine does *not* pass or diffuse into the distilled water. Substances, such as sodium chloride, which thus diffuse through certain membranes were called by Graham *crystalloids*, and substances, such as glue, gelatine, &c., which do not diffuse, *colloids*. The passage of a dissolved substance through a membrane is termed **dialysis**, and the apparatus in which this occurs is called a *dialyser*.

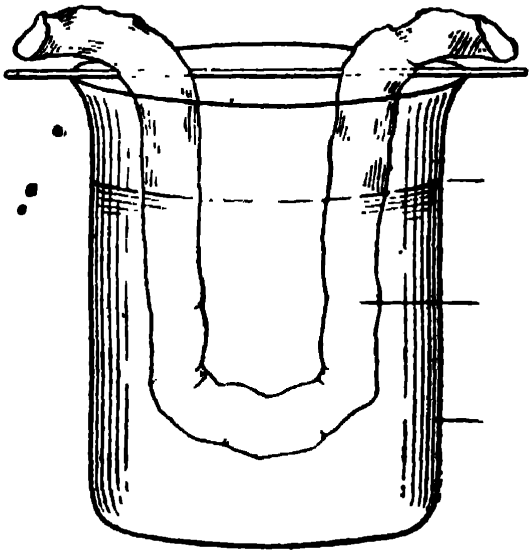


Fig. 89.

On placing the solution of metasilicic acid, obtained in the manner described above, in a dialyser, sodium chloride and hydrogen chloride diffuse into the surrounding water (until a condition of equilibrium between the two solutions is reached); but the metasilicic acid, which is a colloid, remains in the **U**-tube. On carefully withdrawing the outer solution of salt and acid, and putting distilled water in its place, the crystalloids again diffuse until a state of equilibrium is attained, and by repeating these operations until the distilled water is found to remain free from chlorides, the whole of the dissolved crystalloids may be removed from the solution in the **U**-tube.

This tube now contains a clear, apparently homogeneous liquid which is a **'colloidal solution'** of metasilicic acid. If this 'solution' is allowed to evaporate spontaneously it yields a gelatinous amorphous deposit, which does not redissolve completely when the water lost by evaporation is again added, and if the colloidal solution is boiled, or treated with relatively small quantities of various salts, it gives a gelatinous separation of insoluble metasilicic acid.

Many substances, when produced in solution by double decomposition or in other ways, may be obtained in 'colloidal solution,' and may be separated from accompanying crystalloids by the process of dialysis. This 'soluble' form is sometimes called a *hydrosol.* From the 'solutions' thus obtained the colloid is precipitated in a form (sometimes called a *hydrogel*) insoluble in water, by heating the 'solution' or by adding to it an electrolyte (p. 301). Examples are given later (pp. 559, footnote, 614, 704).

The examination of 'colloidal solutions' has led to the conclusion that the substance which appears to be dissolved, and which cannot be separated by ordinary processes of filtration, is really suspended in the liquid, but in an extremely finely divided condition; hence 'colloidal solutions' are often termed *pseudo-solutions* (false or counterfeit solutions) or *colloidal suspensions.*

The behaviour of 'colloidal solutions' is altogether different from that of true solutions. The osmotic pressure of such solutions is relatively very small; the freezing-point and the boiling-point of the solvent are only very slightly changed by the presence of the colloid, and there is no definite boundary line between a saturated and an unsaturated 'colloidal solution.'

'Colloidal solutions' of various metals may be obtained in several ways. One method is to form an electric arc between two wires of the metal which dip below the surface of pure water; under these conditions gold gives a beautiful ruby-red colloidal suspension, while that of silver is yellow, and that of platinum brown. When examined with the ultra-microscope these colloidal suspensions reveal the presence of solid particles of metal, but the particles are so small that they cannot be seen even under the highest powers of any ordinary microscope. Colloidal metals are very active catalysts in many reactions.

Warm, strong solutions of certain colloids (glue, gelatine) set to a jelly, or coagulate, when they are cooled, but regain their fluidity when they are warmed again.

Many substances usually crystalline, if precipitated from solvents in which they are extremely sparingly soluble, appear in a colloidal form. Thus sodium chloride, if formed in dry benzene solution, is often not precipitated, but forms a 'colloidal solution' which appears opalescent. The minute particles are probably unable to dissolve and to give rise to crystals large enough to separate as such, but on the addition of a trace of water aggregation occurs and a deposition of crystals at once takes place.

CHAPTER XXXVI.

Chemical Change.

THE INFLUENCE OF TEMPERATURE.

In the study of solutions, cases have been mentioned in which different molecules 'unite' to form more or less 'stable' substances, such as $Na_2SO_4, 10H_2O$; $K_2SO_4, Al_2(SO_4)_3, 24H_2O$; and so on. In these and in similar cases, however, there is no evidence that the *individual molecules* undergo change during the 'union,' and the formation of hydrates, double salts, and the like, may therefore be regarded rather as examples of physical than of chemical change.

To proceed now to a closer study of chemical change—'a change which results in the formation of new molecules of an element or of a compound' (p. 182)—an attempt may first be made to classify the various reactions already considered in Part I. When this is done the following types may be conveniently distinguished:

1. The combination of two elements to form a compound,

$$H_2 + Cl_2 = 2HCl \qquad 2H_2 + O_2 = 2H_2O,$$

or the reverse of this, the decomposition of a compound into two elements,

$$2HgO = 2Hg + O_2 \qquad 2NH_3 = N_2 + 3H_2.$$

2. The combination of an element and a compound,

$$O_2 + 2CO = 2CO_2 \qquad O_2 + 2H_2SO_3 = 2H_2SO_4,$$

or the reverse of this, the decomposition of a compound into an element and a compound,

$$2PbO_2 = O_2 + 2PbO.$$

3. The decomposition of a compound into two compounds,

$$CaCO_3 = CaO + CO_2 \qquad H_2SO_3 = SO_2 + H_2O,$$

or the reverse of this, the combination of two compounds,

$$CaO + H_2O = Ca(OH)_2 \qquad NH_3 + HCl = NH_4Cl.$$

4. The displacement of one element by an equivalent quantity of another (p. 146),

$$H_2SO_4 + Mg = MgSO_4 + H_2.$$

5. The interaction of an element and a compound, leading to the formation of two new compounds,

$$3O_2 + 2SH_2 = 2SO_2 + 2H_2O.$$

6. Double decomposition, or the interaction of two compounds to form two new compounds (p. 147),

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

7. The interaction of two identical molecules to form two new compounds, a change very similar to double decomposition, as in the formation of silver oxide from the hydroxide (p. 252),

$$AgOH + AgOH = Ag_2O + H_2O.$$

Three other types of change, namely, certain allotropic changes (p. 166), polymerisation (p. 583), and intramolecular change (p. 576), are referred to later.

Now, although nearly all the changes or reactions already considered may be immediately classed as belonging to one or other of these simple types, there would remain some which at first sight might seem to be of a different character. Thus the interaction of copper and hot concentrated sulphuric acid gives rise to three compounds (p. 231), as does also that of copper and nitric acid (p. 246) In these reactions, however, the final results are probably reached by a combination or sequence of two or more of the above simple types of change, and the equation,

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$

for example, may be regarded merely as a summary of the three distinct changes which are represented by the following expressions,

$$Cu + H_2SO_4 = CuO + H_2SO_3$$
$$H_2SO_3 = SO_2 + H_2O$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.^*$$

Even the decomposition of sugar under the influence of heat, a very complex process, which finally leads to the production of carbon, water, and many carbon compounds (p. 116), probably consists of a *sequence* of simple changes, each of which belongs to one of the types given above.

It may be assumed, therefore—and this is the point which it is desired to bring out—that in *all* chemical changes, no matter how complex the final results may be, these results are brought about by *simple reactions between individual molecules in simple proportions.*

Valency and Structure.—It is even possible to go a step further and to attempt a rough representation of the nature

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* The results may also be accounted for by assuming that the following reactions occur,

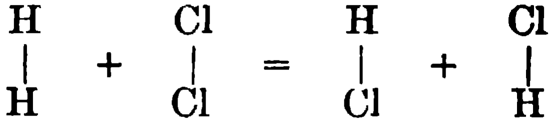
$$Cu + H_2SO_4 = CuSO_4 + 2H \quad \text{and} \quad 2H + H_2SO_4 = 2H_2O + SO_2.$$

of the changes which the individual molecules themselves undergo. The molecule may be regarded as a structure (p. 250) in which the atoms are arranged in some definite manner. The nature of this arrangement, that is to say, the *structure* or *constitution* of the molecule, is intimately connected with the *valencies* of the atoms of which it is composed.

The subjects of valency and structure, which have already been briefly referred to (pp. 206, 250), are most easily presented by making use of a simple mechanical conception. Let it be imagined that the atoms in a molecule are held together by 'hooks' (or bonds); that univalent atoms are provided with one, bivalent atoms with two, tervalent atoms with three 'hooks,' and so on. Then, in order to represent the structure of a molecule in a diagrammatic or graphic manner, the symbols of those atoms which are known to be closely associated are shown as if joined together by their 'hooks' (or bonds). Thus hydrogen being univalent and oxygen bivalent, the *structural* or *graphic formula* of water is written $H-O-H$ or $O{<}^{H}_{H}$; calcium and oxygen being both bivalent, the graphic formula of calcium oxide is written $Ca=O$; hydrogen being univalent and nitrogen tervalent, ammonia is represented by the formula $H-N{<}^{H}_{H}$ or $N\begin{array}{l}\diagup H\\ - H.\\ \diagdown H\end{array}$

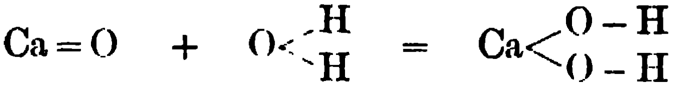
The actual or relative positions of the 'hooks' need not be considered, as the only immediate objects of such structural or graphic formulæ are to show the valencies of the different elements, and to indicate which atoms are directly combined with (or hooked to) one another. In all such formulæ, however, the number of hooks or lines drawn from the symbol of any element must correspond with the known (or presumed) valency of that element in the particular compound which is represented.

Now in any simple chemical change molecules interact in equivalent quantities (p. 176), and the quantities which are equivalent to one another depend on the valencies of the elements or radicles (p. 228) in these molecules. Thus when hydrogen and chlorine unite together the change consists in the displacement of an atom of chlorine by an equivalent quantity of hydrogen, or *vice versâ*, and one atom of chlorine is equivalent to one atom of hydrogen, because the elements are of the same valency,



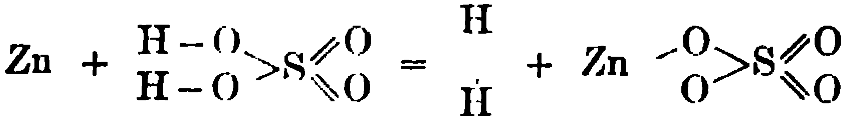
$$\begin{array}{ccccccc} \mathrm{H} & & \mathrm{Cl} & & \mathrm{H} & & \mathrm{Cl} \\ | & + & | & = & | & + & | \\ \mathrm{H} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{H} \end{array}$$

In the combination of calcium oxide and water, there is a simple rearrangement of the atoms to form a new molecule, in which the bivalent calcium atom becomes united to two univalent hydroxyl-groups, instead of to one atom of bivalent oxygen,



$$\mathrm{Ca{=}O} \quad + \quad \mathrm{O}\lt\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array} \quad = \quad \mathrm{Ca}\lt\begin{array}{l}\mathrm{O-H}\\ \mathrm{O-H}\end{array}$$

In the action of zinc on dilute sulphuric acid, the bivalent metal simply displaces an equivalent quantity of hydrogen, without otherwise disturbing the structure of the sulphuric acid molecule (p. 250),



$$\mathrm{Zn} \; + \; \begin{array}{l}\mathrm{H-O}\\ \mathrm{H-O}\end{array}\!\!>\mathrm{S}\lt\begin{array}{l}\mathrm{{=}O}\\ \mathrm{{=}O}\end{array} \; = \; \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H}\end{array} \; + \; \mathrm{Zn}\lt\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\!\!>\mathrm{S}\lt\begin{array}{l}\mathrm{{=}O}\\ \mathrm{{=}O}\end{array}$$

Although, regarded in this light, chemical change seems to be a relatively simple rearrangement of certain atoms, the cause of chemical change is not known. Experiments show that some elements are very inert, while others are very active; but the reason of this great difference in behaviour has not yet been explained. Argon (p. 681), for example, does not form a compound with any element so far as is known, whereas oxygen and chlorine combine readily with most other elements under conditions which are easily attained. Compounds, like elements, differ in activity. Some, such as silica (p. 292), may be classed as relatively inert, or as relatively stable; others, such as sulphuric acid, may be classed as relatively active. In the case of compounds, however, the distinction is more or less arbitrary, and depends on the conditions under which the compound is placed.

The terms stable and unstable, which are so often applied to compounds, solutions, and mixtures, and even to elements, that is to say, to systems generally, are used to express the unreadiness or otherwise with which the specified system undergoes chemical or physical change. It should, however, be borne in mind that many systems appear to be stable merely because they are changing at a rate which is too slow to be observed.

Thus glass is an amorphous substance and apparently quite stable at ordinary temperatures, but in the course of many years it undergoes a very slow spontaneous change, becoming crystalline in structure. Its tendency to crystallise is probably opposed by its enormous viscosity; the particles of glass can move only by overcoming an enormous resistance.

Again, a mixture of oxygen and hydrogen appears quite stable at the ordinary temperature, yet a trace of platinum may cause the gases to unite with measurable speed, and with an evolution of heat which may raise the mixture to its ignition-point.* The gaseous mixture of oxygen and hydrogen is really an unstable one, the spontaneous change of which is opposed by some internal condition analogous to friction or viscosity. The function of the catalyst, platinum (p. 233), has been likened to the effect of a lubricant on the axles and cogs of a machine, although this analogy is certainly a somewhat fanciful one.

THE INFLUENCE OF TEMPERATURE ON CHEMICAL CHANGE.

Although nothing is known as to the cause of chemical change, the *conditions* which hasten or retard chemical change have been carefully studied. Before dealing with the effect of conditions, it must be explained that the **speed or velocity** of a reaction is expressed in terms of the *quantity* of substance which undergoes change in unit time. For any given conditions of temperature, pressure, &c., the speed or velocity depends on two factors: (*a*) on the **velocity coefficient,** which is measured by the rate of transformation of unit mass of substance, and (*b*) on the *quantity* of the substance present in the system considered. The velocity coefficient is independent of the quantity of substance. If, for example, ammonia could be heated under certain fixed conditions, the velocity coefficient of the decomposition would be the same no matter what volume of the gas were taken; that is to say, unit mass of substance would undergo change at the same rate, or the same fraction of the substance would be decomposed in unit time. The speed or velocity of the decomposition, however, would depend on the quantity of the gas, as explained later (p. 355).

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* The ignition-point is that temperature at which the initial flameless combination heats the mixture until it inflames.

At this stage it is unnecessary to consider in what way the speed or velocity of a reaction depends on quantity, and in speaking of the speed of any reaction it may be assumed that the quantity of substance is constant, and that the speed is proportional to the velocity coefficient

Now one of the more important conditions which determine the speed of a chemical change is that of temperature. At very low temperatures, as, for example, at that of boiling liquid air (about − 183°), most chemical changes either do not occur or else take place very slowly. A reaction which progresses slowly at ordinary temperatures generally takes place more rapidly as the temperature rises, the speed or velocity of the change being often just about doubled for a rise in temperature of 10°. But at higher temperatures still a point may be reached at which the original reaction does not occur to any appreciable extent.

Thus at − 80° chlorine has no action on phosphorus, but at ordinary temperatures the two elements combine rapidly. Mercury and oxygen do not combine with any appreciable speed at ordinary temperatures, but do so at about 300°; at much higher temperatures, say at 600°, these elements have no appreciable action on one another. Again, hydrogen and oxygen do not unite to an appreciable extent at ordinary temperatures, but at 540° they form steam with appreciable speed; at 560°, if mixed in suitable proportions, they combine instantaneously and practically completely, with explosive violence; at 2000° the union is less nearly complete; at still higher temperatures more and more of the hydrogen and oxygen remain free, and doubtless at the highest attainable temperatures hardly any combination between these elements would take place. On the other hand, nitrogen and magnesium do not react with appreciable speed at temperatures below a red-heat, but the compound then formed is stable even at the highest temperature of the electric furnace.

These examples show that the influence of temperature on chemical change is very great, and the apparent contradictions which they present are explained as follows: Many chemical changes are *reversible*; that is to say, the products of a given change may react under suitable conditions and give the original substances (pp. 86, 107). A change in temperature, therefore, may not only alter the speed of a given reaction, but it may at the same time lead to a more or less complete *reversal* of that reaction by increasing the speed of the opposed change to an even greater extent.

Thus when mercury is heated in the air combination with oxygen takes place slowly at about 300°, and the speed of the reaction increases as the temperature rises, say to 350°; at the same time this rise in temperature brings about an increasing tendency for the product to decompose into its constituents. As the temperature rises further, both the speed of formation and the speed of decomposition become greater, but the speed of decomposition increases much the more rapidly. The result is that when a particular temperature is reached, the speed of decomposition becomes greater than the speed of formation; at this temperature the mercuric oxide decomposes and the two elements do not combine to any appreciable extent.

In the case of the combination of hydrogen and oxygen the influence of temperature may be explained in a similar manner. At ordinary temperatures the speed of combination is inappreciable, but increases as the temperature rises; at 560° the combination, which below this temperature takes place without the production of flame, becomes an *explosion;* the heat evolved by the more rapid union heats the mixture to its *ignition-point*, that is to say, the point at which it inflames. At 2000° the speed of the reverse reaction, namely, the decomposition of the steam into its elements, is appreciable; at higher temperatures still the speed of this decomposition may become so much greater than the speed of formation that the union is very incomplete.

OTHER CONDITIONS WHICH INFLUENCE CHEMICAL CHANGE.

The influence of pressure on chemical change is considerable, and is of especial importance where solids are being formed from, or are reacting with, liquids or gases; but these cases cannot at present be discussed.

In addition to temperature and pressure, the physical state of a substance is a factor of much importance in conditioning chemical change. Reactions between solid substances usually occur very slowly, and as a rule it is necessary that at least one of the substances should be present in a gaseous, liquid, or dissolved state. Hence highly insoluble solid substances which cannot easily be melted, as, for example, barium sulphate, are inert under ordinary conditions. It is perhaps the usual rule that a solid only takes part in chemical change in so far as it dissolves or volatilises, in which case it may be supposed to undergo chemical change only in the dissolved or gaseous state.

CHAPTER XXXVII.

Chemical Change.

THE HEAT OF REACTION.

It has already been pointed out (p. 136) that when a chemical change occurs in any given system, the quantity of energy contained in the final, is different from that contained in the original, system; a part of the chemical energy is transformed into heat, light, or some other form of energy which is dissipated, unless the system is isolated (footnote, p. 135).

When a chemical change can be so regulated that no form of energy except heat flows from the system to the exterior (or *vice versâ*), then this output of heat represents the decrease in the internal energy of the system, and may be measured, the quantity is expressed in calories (footnote, p. 136) and is known as the *heat of reaction*, but in the case of the production of a compound from its constituent elements it is termed the *heat of formation* (p. 136) of the compound.

In the practical determination of the heat evolved during a chemical change, the materials are usually surrounded by a considerable mass of water, so that the system starts at approximately the temperature of the surroundings. The chemical change is then started in a suitable manner,* and as the change proceeds it gives out heat to, or absorbs heat from, the surrounding water, the temperature of which rises or falls in consequence. The heat capacity of the whole apparatus and the contained water is known, and thus the heat required to produce the observed rise in temperature is easily calculated, for the heat capacity of the material undergoing the chemical change is almost negligible in comparison with that of the apparatus. Since much heat might be lost to the surroundings if the apparatus were at any time much hotter or colder than the outside air, it is necessary so to arrange the conditions that the observed rise or fall in temperature is small, as a rule not more than one or two degrees.

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* As, for example, by 'sparking' (p. 298), or with the aid of a platinum wire heated electrically.

It is evident, therefore, that the heat of reaction, then measured, is the heat evolution or absorption for the particular case where the reacting substances (in gram-molecules) and the products have the same (generally atmospheric) temperature; consequently in all cases the term '**heat of reaction**' is understood to imply these conditions.

When examined in this way, reactions may be classed either as *exothermic*, when the heat of reaction is positive, or as *endothermic*, when the heat of reaction is negative.

Now, *broadly speaking*, those reactions which take place very violently are those which are strongly exothermic, and compounds which are formed from their elements by strongly exothermic reactions are generally stable On the other hand, those compounds which are produced from their elements by endothermic reactions are usually easily decomposed, and are often extremely explosive.*

Further, a strongly exothermic reaction *often* proceeds spontaneously, or, if once started, often continues without any further external supply of heat or other form of energy; an endothermic or a feebly exothermic reaction, however, *often* ceases unless there is a continuous supply of external energy to the system.

The latter general principle, to which, however, there are *innumerable exceptions*, may be illustrated by the following examples:

1. When *dry* hydrogen sulphide is passed over *dry* iodine

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* It must not be thought that an 'explosive' is necessarily an endothermic compound Gunpowder, for example, is an explosive because the system is capable of undergoing a strongly exothermic reaction during which a large volume of gaseous products is suddenly generated (footnote, p. 241).

(p. 412) at ordinary temperatures no appreciable reaction occurs. When, however, iodine is added to an aqueous solution of hydrogen sulphide a rapid action occurs, sulphur is deposited, and hydrogen iodide remains in solution.

The reason of this difference is that the formation of hydrogen iodide from iodine and hydrogen sulphide at ordinary temperatures is an endothermic reaction, which may be represented by the expression,

$$H_2S + I_2 = 2HI + S - 7300 \text{ calories.}$$

To put this in another way: the heat of formation of 1 gram-molecule of hydrogen sulphide is greater than the heat of formation of 2 gram-molecules of hydrogen iodide to the extent of 7300 calories, and the endothermic reaction expressed above does not occur spontaneously. When, however, water is present in excess, the final results may be represented as follows,

$$H_2S(\text{aqueous solution}) + I_2 = 2HI(\text{aqueous solution}) + S + 17{,}100 \text{ calories,}$$

$$\text{or}\quad H_2Saq\,^{*} + I_2 = 2HIaq + S + 17{,}100 \text{ calories;}$$

that is to say, the reaction in aqueous solution is strongly exothermic, and now proceeds without a supply of external energy. So much heat is developed by the solution of the hydrogen iodide that the presence of water in excess completely alters the character of the reaction.

2. At 100° copper is not attacked by dilute sulphuric acid, nor by oxygen at an appreciable rate, and sulphuric acid is not attacked by oxygen. Yet when copper is placed in dilute sulphuric acid and oxygen is bubbled through the liquid, heated at 100°, the copper displaces hydrogen from the acid, forming copper sulphate, and water is simultaneously produced by the union of the hydrogen with the gaseous oxygen.

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* The expressions H_2Saq and $2HIaq$ signify that the quantities of the compounds here represented are dissolved in a quantity of water sufficient to give the maximum thermal change (heat of solution, p. 308).

The explanation of these facts is similar to that just given in the first example. The system [Cu, H_2SO_4aq] does not change spontaneously into [$CuSO_4aq + H_2$], but when oxygen is added to the system the reaction,

$$2Cu + 2H_2SO_4aq + O_2 = 2CuSO_4aq + 2H_2O,$$

proceeds at an appreciable speed. The combination of the hydrogen and oxygen to form water gives so much additional heat that the system [2Cu, $2H_2SO_4aq$, O_2] changes spontaneously.

3. A solution of potassium permanganate (p. 450) is not acted on by zinc, or by dilute sulphuric acid, or by hydrogen, at ordinary temperatures, but when zinc and sulphuric acid are placed together in a solution of potassium permanganate the latter is reduced, and, with excess of zinc and acid, the pink colour of the solution ultimately disappears.

From these examples it may be inferred that in many cases at any rate a spontaneous chemical change in a system occurs only when the sum of the heats of reaction is positive and sufficiently large; also that a given final result may often be attained by combining in one system two or more reactions, one or more of which may be incapable of proceeding alone.

The Nascent State.—It has just been mentioned that although potassium permanganate is not acted on by zinc *or* by dilute sulphuric, yet it is decomposed or reduced in contact with zinc *and* dilute sulphuric, acid. Presumably, therefore, it is reduced by the hydrogen which is generated during the interaction of the metal and the acid. But when hydrogen from a gas-holder or other vessel is bubbled through a solution of potassium permanganate, the gas does not act on the solution in any way whatever.

These facts were at one time explained by assuming that when zinc displaces hydrogen from sulphuric acid, the hydrogen is actually but momentarily liberated in the form of *atoms;* further, that these atoms are much more active than the molecules, H_2, of which gaseous hydrogen is known to consist (p. 196), and that it is these active atoms which attack the potassium permanganate. In accordance with this assumption, hydrogen in this active atomic state was called **nascent** hydrogen, or hydrogen in the nascent condition (*nascens*, beginning to exist), since it was only at the moment of its liberation (or at the beginning of its existence) that it occurred in this condition.

Many other cases are known in which so-called *nascent hydrogen*, that is to say, hydrogen which is generated in presence of a substance, brings about a reaction which ordinary gaseous hydrogen, or molecules of hydrogen, cannot accomplish. Several other elements, such as oxygen and chlorine, are also known to act rapidly on certain substances when they are *generated* in contact with them, but not when the elements are prepared separately and then brought into contact with these substances. The terms *nascent* oxygen, *nascent* chlorine, &c. were therefore used in relation to the elements generated under such conditions.

Convenient though it may be to use the term 'nascent' to express briefly certain conditions, it is not necessary to assume that the action of a 'nascent' element is due to its existence in the atomic state. The occurrence of a reaction in one system and its non-occurrence in a totally different system requires no such explanation.

Just as the heat of reaction of the system $[H_2Saq, I_2]$ is much greater than that of the system $[H_2S, I_2]$, owing to the occurrence of a physical change which is attended by a development of heat (the heat of solution of 2HI), so may the heat of reaction of the system containing zinc, dilute sulphuric acid, and potassium permanganate be much greater than that of the system consisting of hydrogen and potassium permanganate, owing, for example, to the development of heat which accompanies the formation of a solution of zinc sulphate from zinc and dilute sulphuric acid.

In the following pages, therefore, the term 'nascent' is applied to an element which is (presumably) generated in some reacting system, but which, instead of being set free, immediately takes part in some other reaction in that system and does not appear as a final product. The term 'nascent' must not be taken to imply that the element so qualified is in the atomic state.

A consideration of the connection between the heat of reaction and the occurrence of chemical change led Berthelot (in 1867) to the assumption that every spontaneous chemical reaction proceeds in that direction which leads to the maximum development of heat (*Berthelot's principle of maximum heat*). The heat of reaction was thus regarded as a measure of the chemical *affinity* of a reaction; that is to say, it was thought that the power urging a reaction in a certain direction was proportional to the heat of the reaction. It is now recognised that such a view is untenable, since innumerable cases are known in which endothermic reactions occur spontaneously. Nevertheless it is generally true that where the heat changes are very great, the reactions proceed mainly in the direction in which heat is evolved.

The identification of heat as a form of energy drew attention very closely to this aspect of chemistry, and the fundamental fallacy in identifying the power behind a chemical change with the heat of reaction is not very easily grasped, until it is thoroughly realised that the amount of heat which is *given out* by a system is not necessarily the same quantity as that which is *produced within* the system. Usually any chemical change results in the system being able to hold less or more heat, as such, than it held before the change, so that *less or more heat than is actually produced, as such, within the system* flows to the exterior.

At the absolute zero of temperature no material contains energy in the form of heat; hence at this temperature the whole of the heat developed during a chemical reaction would flow out to the surroundings and appear as 'heat of reaction.' At any other point on the thermometric scale, however, any material contains that quantity of heat which it would yield if cooled to the absolute zero.

If, therefore, two substances, A and B, react to form a third, C, then, in general, the total heat they would give to the surroundings, if cooled to the absolute zero from the temperature of experiment, varies with that temperature. For the sake of clearness, assume that the quantities of heat they contain in virtue of their temperature, say at 0° C. or 273° absolute, are respectively, A, 20 calories; B, 25 calories; and C, 50 calories. The total for A and B = 45 calories, which is 5 calories less than C contains at the same temperature. Thus were A and B to change into C in a bath maintained at 0°, then if the chemical change produced no appreciable amount of heat, the system would absorb 5 calories from the bath, and the heat of reaction would be −5 calories. If the chemical change produced less than 5 calories of heat, the heat of reaction would still be negative and the reaction still 'endothermic,' and only when the chemical change produced more than 5 calories would the heat of reaction become positive. It is obvious, therefore, that chemical affinity cannot be measured, even approximately, by the heat evolved, but that when the heat of reaction is so great that changes in the heat capacities of the reacting substances may be neglected in comparison, then the heat evolution may be a rough measure of chemical affinity.

Thus in the case of reactions between solids, heat of reaction is probably more nearly a measure of chemical affinity than in the case of liquids or gases, as the specific heats of solids are very nearly additive quantities, and the products therefore have nearly the same heat capacity as the original substances.

There are purely thermo-dynamic reasons for believing that at the absolute zero the heat of reaction is a measure of the *affinity* of a change, i.e. the maximal external work which could be obtained from the change.

THE LAW OF HESS.

The direct method given above (p. 337) for the measurement of the heat of reaction is only applicable in the case of those reactions (exo- or endo-thermic) which continue, when once they have been started, without a further supply of external energy. It is possible, however, by indirect methods to measure the heat of reaction in other cases. Such measurements are based on an application of a general law (**the law of Hess**) that '*the change in internal energy resulting from the conversion of one system into another under given initial and final conditions is constant, and is independent of all intermediate physical and chemical changes.*' As an illustration of this law the following example may be given.

Starting from a system of 1 gram-molecule of ammonia and 1 gram-molecule of hydrogen chloride, and an indefinitely large weight, say 100 litres, of water, all under certain conditions of temperature and pressure, it is possible to prepare a dilute aqueous solution of ammonium chloride in two ways. (1) By combining the two gases and then dissolving the ammonium chloride in the water. (2) By dissolving the two gases separately in two equal or unequal parts of the water and then mixing the solutions. Experiments have shown that the heat development is the same in the two cases if the final conditions of the solution are the same. In the first case the combination of the two gases gives + 42,100 calories, and the solution of the solid ammonium chloride is attended by an absorption of − 3900 calories, so that the total heat development is + 38,200 calories. In the second case the solution of the ammonia gives + 8400 calories, and the solution of the hydrogen chloride + 17,300 calories, and a further heat development of + 12,300 calories occurs on the solutions being mixed, so that the total is + 38,000 calories, The results of such experiments may be expressed as follows,

$$NH_{3(gas)} + HCl_{(gas)} = NH_4Cl_{(solid)} + 42,100 \text{ cals.}$$
$$NH_4Cl_{(solid)} = NH_4Cl_{(aq)} - 3900 \text{ cals.}$$
$$NH_{3(gas)} + HCl_{(gas)} = NH_4Cl_{(aq)} + 38,200 \text{ cals.}$$

Since the heat of reaction represents the difference between the total internal energies of the original and final systems, while it is impossible to determine the whole internal energy of any substance or system, these *differences* may be ascertained experimentally and used to determine others which cannot be measured directly.

The heat of formation of hydrogen sulphide, for example, cannot be measured directly because the two elements only combine very slowly and incompletely, and under conditions which preclude thermal estimations; nevertheless the value may be deduced indirectly in the following manner.

The heats of formation of water and of sulphur dioxide may be directly determined by burning weighed quantities of the elements in excess of oxygen; the values are respectively + 68,400 calories and + 71,100 calories.

The signs 2[H] and [O] being employed, for example, to represent the unknown internal energies of a gram-molecule of hydrogen and of a gram-atom* of oxygen respectively, in calories, then from the experimental data in the last paragraph,

$$(a)\quad 2[H] + [O] = [H_2O] + 68,400 \text{ cals.}$$
$$(b)\quad [S] + 2[O] = [SO_2] + 71,100 \text{ cals.}$$

The heat of combustion of hydrogen sulphide in excess of oxygen may also be determined experimentally, and may be expressed thus,

$$(c)\quad [H_2S] + 3[O] = [H_2O] + [SO_2] + 136,710 \text{ cals.}$$

*** In these and other thermo-chemical expressions it is often more convenient to represent the quantities of the elements concerned by gram-atoms instead of by gram-molecules.**

From these it is required to determine the value of

$$(d)\quad 2[H]+[S]-[H_2S].$$

It is merely necessary to substitute in (d) the values of $2[H]$, $[S]$, and $[H_2S]$, given by (a), (b), and (c).

From (a) $\quad 2[H]=[H_2O]-[O]+68{,}400$ cals.
From (b) $\quad [S]=-2[O]+[SO_2]+71{,}100$ cals.
Therefore $\quad 2[H]+[S]=[H_2O]-3[O]+[SO_2]+139{,}500$ cals.
From (c) $\quad [H_2S]=[H_2O]-3[O]+[SO_2]+136{,}710$ cals.

Hence, by subtraction,

$$2[H]+[S]-[H_2S]=+2790 \text{ cals.},$$

or the heat of formation of hydrogen sulphide (one gram-molecule) from free hydrogen and solid sulphur is +2790 calories.*

The heat of formation or heat of reaction is generally determined at ordinary room temperature, but the result is not independent of the temperature by any means. If, however, the heat of reaction at any given temperature is known, as well as the specific heats of all the reacting substances and products, then the heat of reaction at any other temperature may be calculated.

In the case where any changes of state occur between the two temperatures, the latent heats of the changes must also be considered.

Thus the heat of the reaction,

$$2H_2+O_2=2H_2O_{\text{liquid}} \text{ (at } 0^\circ\text{)},$$

is $\quad 2\times 68{,}400$ cals., or $Q=136{,}800$ cals.

Q_1, or the heat required to raise 2 gram-molecules of hydrogen + 1 gram-molecule of oxygen from 0° to 100°, is

$$2\times 100\times 6{\cdot}823 \text{ cals.}\dagger + 100\times 6{\cdot}823 \text{ cals.}=2047 \text{ cals.}$$

Q_2, or the heat required to raise 2 gram-molecules of water at

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* The heats of formation of compounds are often expressed in large calories, units 1000 times as great as the small calories (footnote, p. 135) used above.

† 6·823 cals. is the *molecular heat* of hydrogen under constant pressure, that is, the heat required to raise the temperature of 1 gram-molecule of hydrogen 1° under constant pressure. The molecular heat of oxygen is also 6·823 cals.

0° to water at 100° + the heat required to convert this quantity of water at 100° into steam at 100°, is

$$2 \times 18 \times 100 \text{ cals.} + 2 \times 18 \times 536{\cdot}4 \text{ cals.}^{*} = 22{,}910 \text{ cals.}$$

Hence the heat of the reaction,

$$2H_2 + O_2 = 2H_2O_{\text{vapour}} \text{ (at } 100°\text{)}$$

is

$$Q + Q_1 - Q_2 = 115{,}937 \text{ cals.}$$

Since the heat of reaction depends on the physical state of a substance, it follows that the different forms of an element have different heats of reaction under similar conditions; thus the heat of formation of sulphur dioxide from rhombic, is less than that from monoclinic, sulphur. In like manner, sugar charcoal, graphite, and diamond have different heats of reaction when they are converted into carbon dioxide.

The difference between the heats of formation of CO_2 from one gram-atom of graphite and charcoal respectively evidently represents the difference in the internal energies of these two allotropic forms—in other words, is equal to the heat of the allotropic transformation.

CHAPTER XXXVIII.

Chemical Equilibrium.

THERMAL DISSOCIATION.

One common result of an increase in temperature is to bring about the permanent decomposition of complex molecules into simpler ones, as in the decomposition by heat of potassium chlorate, copper nitrate (p. 242), and tartaric acid (p. 282). In many cases, however, the decomposition which occurs when the temperature is raised is reversed when the temperature is lowered again slowly, provided that the products remain in contact with one another: substances (elements or compounds) which are affected in this way are said to undergo **thermal dissociation.** Some typical cases of thermal dissociation may now be studied.

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* The latent heat of steam.

Dissociation of Ammonium Chloride.—When ammonium chloride is heated it is converted into a vapour which condenses again when cooled, giving pure ammonium chloride (p. 246). Now the density of this vapour determined at temperatures above 350° and at atmospheric pressure is found to be about 13·3; that is to say, the vapour is about 13·3 times heavier than an equal volume of hydrogen under the same conditions.* But the molecular weight of ammonium chloride, NH_4Cl, is 53·5 (14 + 4 + 35·5), and therefore if the vapour consisted of NH_4Cl molecules its density would be $\frac{53 \cdot 5}{2} = 26 \cdot 7$ (p. 197).

In order to account for the unexpected (or abnormal †) result for the vapour density which is obtained experimentally, and which is only half the calculated value, it must be concluded that every NH_4Cl molecule has decomposed into *two* molecules, probably into NH_3 and HCl. If this were so, then, since equal numbers of molecules occupy equal volumes under the same conditions of temperature and pressure, the volume of the vapour obtained from a given weight of ammonium chloride would be *twice* as great, and its density *half* as great, as would be the case if the vapour consisted entirely of molecules of NH_4Cl; that is to say, the experimental results would be satisfactorily accounted for.

This conclusion, based on the results of vapour density determinations, may be confirmed experimentally in the following manner: A small quantity (say 1 gram) of ammonium chloride is placed in the glass tube of the apparatus shown in fig. 64 (p. 167) and heated until some of it vaporises. A stream of air is then gently blown through the inner porous earthenware tube (*a*), and a damp red litmus-paper is held in the escaping gas; the colour of the litmus soon changes to blue. At the same time a piece of damp blue litmus-paper previously placed inside the glass tube becomes red.

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* The method used in determining the vapour density is described later (p. 371).

† Compare footnote, p. 370.

These results show that the vapour obtained by heating ammonium chloride is really a *mixture* of ammonia and hydrogen chloride. In the given apparatus the two gases have merely been separated from one another to a small extent by the process of gaseous diffusion, in consequence of their different densities. As the density of ammonia, NH_3, is 8·5, and that of hydrogen chloride, HCl, is 18·2, the rate of diffusion of the former is greater than that of the latter in the ratio of $\frac{1}{\sqrt{8\cdot5}} : \frac{1}{\sqrt{18\cdot2}}$ (p. 167). Therefore, as the two gases are under the same partial pressure (pp. 164, 167), a greater number of molecules of ammonia than of hydrogen chloride passes through the earthenware tube in a given time. Hence, since the mixture in the glass tube originally contains equal volumes of the two gases, after diffusion has occurred, the diffused gas contains some free ammonia, and the undiffused gas some free hydrogen chloride. If, on the other hand, the gases are not separated from one another while the mixture is still at a fairly high temperature, they unite to form pure ammonium chloride.

These facts prove that ammonium chloride undergoes thermal dissociation, a reversible change expressed by the following equation,

$$NH_4Cl \longleftrightarrow NH_3 + HCl.$$

In absence of every trace of water, ammonium chloride may be vaporised without dissociation taking place (its vapour density is then 26·6), and ammonia and hydrogen chloride may be mixed together without any combination taking place. Many other cases are known in which the presence of a *trace* of water is necessary for the occurrence of a reaction (decomposition or combination). Water, therefore, may be said to act as a catalytic agent in many chemical changes. A mixture of perfectly dry carbon monoxide and oxygen, for example, does not explode when it is sparked, although it does so in presence of a trace of water.

Dissociation of Nitrogen Tetroxide.—The almost colourless crystalline compound nitrogen tetroxide, N_2O_4 (p. 216), melts at − 12° to a pale-yellow liquid (b.p. 22°), which gives a dark reddish-brown vapour when it is warmed; these changes are reversed when the vapour is cooled.*

The results of vapour density determinations show that this change in colour is due to thermal dissociation. At 150° (under atmospheric pressure) the density of the (brown) gas is 23, which corresponds with that of a compound of the molecular formula NO_2 (M.W. = 46). At 26°, however, the density is 38, whereas that calculated for a compound of the molecular formula N_2O_4 is 46. Hence at 26° the vapour consists of a mixture of molecules of N_2O_4 and NO_2. Between 26° and 150° the density gradually diminishes, but it becomes and remains constant for any constant temperature and pressure.

These results prove that colourless nitrogen tetroxide undergoes thermal dissociation, giving a brown gas, nitrogen dioxide, NO_2,

$$\underset{1\ \text{vol.}}{N_2O_4} \longleftrightarrow \underset{1\ \text{vol.}\ +\ 1\ \text{vol.}}{NO_2 + NO_2}.$$

At temperatures considerably above 150° the molecules NO_2 dissociate into oxygen and nitric oxide, and at extremely high temperatures nitric oxide dissociates into its elements (p. 299).

Dissociation of Calcium Carbonate.—When calcium carbonate is heated in an open vessel at a dull-red heat, say at 750°, it is *completely* decomposed into carbon dioxide and calcium oxide, but when it is heated in a closed vessel, so that the carbon dioxide cannot escape, a very different result is obtained. This can be proved by heating a considerable quantity of the compound in a metal tube which is connected with a pressure-gauge. At 517 decomposition commences, and continues until the pressure of the carbon dioxide becomes 27 mm., but the pressure, and therefore the volume, of the liberated gas remain constant so long as the temperature remains constant. On the solid being heated more strongly, however, a further quantity of gas is liberated; thus at 610° the pressure rises to, and again becomes constant at, 47 mm.; at 812° the pressure becomes equal to normal atmospheric pressure. At higher temperatures still, more gas is liberated, but for every (constant) temperature the pressure of the carbon dioxide reaches a constant value. On the products being cooled *slowly*, the carbon dioxide is gradually absorbed, until the pressure corresponding with the lower temperature is reached; below 547 practically the whole of the gas is absorbed.

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* If a glass bulb filled with the reddish brown gas at ordinary temperatures is immersed in a good freezing mixture, the contents of the bulb become almost colourless.

These experiments prove that calcium carbonate undergoes thermal dissociation,

$$CaCO_3 \longleftrightarrow CaO + CO_2.$$

Many other compounds, as, for example, hydrogen iodide (p. 423) and phosphorus pentachloride (p. 544), undergo thermal dissociation.

Dissociation of Sulphur.—The atomic weight of sulphur is 32; the value cannot be more than 32 because 1 gram-molecule of many sulphur compounds contains only 32 grams of sulphur (compare p. 198). Now the vapour density of sulphur* at temperatures near its boiling-point (440°) and at atmospheric pressure is about 128, which corresponds with the molecular weight 256; hence at such temperatures the molecule of sulphur is S_8 ($32 \times 8 = 256$). As the temperature at which the vapour density is observed is raised, the value found continually diminishes until it becomes constant at about 1700°, and is then 32, which corresponds with the molecular weight 64 and the molecular formula S_2. When the vapour at 1700 is allowed to cool, the molecules S_2 combine to form molecules S_8, and finally solid sulphur is again obtained. This dissociation is expressed by the equation,

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* Determined by the method described later (p. 371).

CHEMICAL EQUILIBRIUM.

In all cases of dissociation, a decomposition which begins by taking place with considerable speed at a particular temperature *seems* to cease after a certain time when the products of dissociation are not allowed to escape. Thus in the case of nitrogen tetroxide the density becomes and remains perfectly constant under fixed conditions when only a portion of the gas is decomposed, and dissociation is incomplete over a considerable range of temperature. Similarly, when calcium carbonate is heated at, say, 610° in a closed vessel, the pressure of the carbon dioxide attains a constant value, at which it remains no matter how much calcium carbonate is taken and however long the heating is continued.

Now it cannot be believed that changes which commence with considerable speed at a particular temperature proceed only for a time and then come to an end. It seems much more reasonable to assume that the *apparent* cessation of change is really the result of two opposed reactions which are taking place with equal speed; that is to say, all change seems to be at an end because, in any given time, the weight of substance which is dissociated is exactly the same as the weight of that substance which is formed by the reverse reaction.

This conclusion is fully confirmed by other experimental evidence. It can be proved that the changes are reversible and may be made to proceed in either direction; also that, starting with a system consisting wholly of the undissociated molecules *or* with one consisting wholly of the products of dissociation, the same final result is ultimately reached if the different systems are brought to the same conditions of temperature and pressure.

When, for example, (*a*) ammonium chloride is slowly heated to 300°, and (*b*) equal volumes of hydrogen chloride and ammonia are mixed at 500° and then cooled to 300°, the pressure being the same in both cases, the final systems have the same vapour-density, and therefore contain molecules of NH_4Cl, HCl, and NH_3 in the same proportions in the two cases.

A system, such as one of the above, the composition of which remains constant owing to the occurrence of two opposed reactions, is said to be in a **state of equilibrium.** The study of the conditions which determine the chemical equilibrium of a system is of the utmost importance.

THE INFLUENCE OF CONCENTRATION ON CHEMICAL EQUILIBRIUM.

In the examples of reversible chemical change classed as thermal dissociations, a state of equilibrium is attained by the system, under constant conditions, owing to the occurrence of two opposed reactions which are taking place with equal speeds. Now under those conditions at which dissociation begins, the reverse reaction (combination) must be taking place, for the moment, at a relatively smaller speed, otherwise decomposition would not be progressive. At the state of equilibrium, however, the speeds of these two reactions have become equal. It is now necessary to consider how this equality is established.

For this purpose, attention may first be drawn to the reversible reaction which takes place between iron and steam. It has already been shown that steam is decomposed by iron at a red-heat (say at $t°$), with formation of an oxide of iron, Fe_3O_4, and liberation of hydrogen; on the other hand, this same oxide of iron is reduced by hydrogen at a red-heat ($t°$), with formation of iron and steam; these reversible reactions are expressed by the equation,

$$3Fe + 4H_2O \longleftrightarrow Fe_3O_4 + 4H_2.$$

Now it is clear that in the first case the speed of the reaction expressed by reading the equation from left to right *must be very much greater than that of the opposed change,* whereas in the second case the relative speeds of these two reactions must be reversed. The question is, how is this reversal brought about? Consider what would occur if some iron and water were heated together in a closed vessel at a red-heat (t°). At first a reaction commences which is expressed by reading the above equation from left to right, and after some time a certain proportion of the steam will have been decomposed. As this decomposition progresses and the quantity of steam present gets less and less, the weights of oxide of iron and of hydrogen which are formed in unit time under given conditions will also continually decrease. But as soon as oxide of iron and hydrogen have been formed the reaction expressed by reading the equation from right to left also commences. At first the weights of iron and of steam which are produced in unit time can only be small, because so little oxide of iron and hydrogen are present in the vessel, but as the quantities of the latter increase, so also will the weights of the iron and steam which are produced in unit time.

Hence, starting with a system of iron and steam at any constant temperature at which the reaction is reversible, the speed of the one change gradually diminishes, while that of the other gradually increases. The consequence is, that after the system has been kept for a sufficient time at the constant temperature, the two opposed changes will be taking place with equal velocity and a condition of equilibrium will have been attained, the composition of the system remaining constant.

As this condition of equilibrium is the result of two reactions which 'balance' one another, reversible reactions are often termed **balanced reactions**.

Now if, when equilibrium has been attained, some of the hydrogen (but not the steam) present in the vessel could be removed, the weight of oxide reduced in unit time would be less than before; that is to say, the removal of the hydrogen would diminish the speed of the reaction from right to left, but would have no effect on the speed of the reaction from left to right. Therefore, if from the very first the whole of the hydrogen were removed as fast as it was produced, the reaction would proceed from left to right as quickly as before, but the reverse change could not take place at all. This is what happens when steam is passed over red-hot iron; in this process the hydrogen is swept away from the oxide by the current of steam as fast as it is formed. In an exactly parallel manner, the removal of some of the water vapour from the tube when equilibrium has been reached would disturb the equilibrium, and the weight of water decomposed in unit time would be decreased, while the velocity of the reaction from right to left would not be affected. Consequently heated oxide of iron may be completely reduced by passing a stream of dry hydrogen over it, because the water vapour is swept away from the iron and the reverse reaction cannot take place.

The general principle illustrated by this case is one of very great importance, as it applies in all reversible or balanced reactions, including those classed as thermal dissociations.

Chemical change takes place between individual molecules which come into contact with one another or which themselves decompose. When, therefore, the number of molecules of a gas, liquid, or dissolved substance in a given space or volume is increased, these molecules come into contact with one another more frequently in a given time, and greater numbers of them undergo change. To put this in another way: if the **molecular concentration** of a gas, liquid, or dissolved solid* is defined as *the number of gram-molecules of that substance in unit volume*, and the **speed** or **velocity** of a reaction is defined as *the total change in molecular concentration of one of the changing substances in unit time*, then any increase or diminution in the molecular concentration of a substance which is taking part in a reaction produces an increase or diminution in the speed of that reaction.

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* The molecular concentration of a solid, *as such*, may be taken as constant.

Applying this conclusion to the reversible reaction just considered, it may now be stated that, starting from a closed system of iron and steam, the speeds of the two reactions ultimately become the same because the molecular concentration of the steam gradually diminishes, while that of the hydrogen gradually increases. Similarly in cases of thermal dissociation; the molecular concentration of one or of both the products of dissociation, which at first is *nil*, gradually increases until it reaches such a value that the speed of combination equals the speed of decomposition.

It follows therefore that if, at the state of equilibrium, the molecular concentration of one of the substances is changed by any means, the state of equilibrium is also disturbed. Similarly, if one of the products of a reversible change is added to a system which is giving that product, the reaction does not proceed so far as it otherwise would, because the limiting molecular concentration of that product is reached at an earlier stage. Thus when ammonium chloride is heated in a vessel previously filled with ammonia, or with hydrogen chloride, the dissociation is less, for a given temperature, than when the vessel is filled with air; in like manner, the dissociation of calcium carbonate is more limited when the compound is heated in an atmosphere of carbon dioxide than when it is heated in the air.

Le Chatelier's Rule.—Systems in which solids are in equilibrium with gases or solutions, or in which liquids are in equilibrium with gases or vapours, are known as systems in *heterogeneous equilibrium.* In all such systems, of the two reversible physical or chemical changes which are taking place, one is exothermic, the other endothermic. Thus in the equilibria represented by solid ⟷ vapour, or liquid ⟷ vapour, the change from left to right is exothermic, that from right to left endothermic. In the equilibrium solid ⟷ solution, as already shown (p. 308), the change from left to right may be either exothermic or endothermic, but the change from right to left is then endothermic or exothermic as the case may be. Similarly in the case of reversible chemical changes, such as the dissociation of calcium carbonate.

Now in all systems in equilibrium, whether the system is heterogeneous or homogeneous, the result of a change in the conditions is expressed by **Le Chatelier's rule,** which may be stated in the following form: '*When one or more of the factors determining an equilibrium, namely, pressure, temperature, or concentration, is changed, then the equilibrium automatically alters in the direction which tends to neutralise the effect of that change.*'

If, for example, the temperature of the system is raised by the application of external warmth, then those changes will occur within the system which tend to lower the temperature, that is, those associated with absorption of heat.

Thus calcium carbonate dissociates with absorption of heat; consequently when a system containing calcium carbonate in equilibrium with lime and carbon dioxide is raised in temperature, more calcium carbonate dissociates, because in so doing it tends to restore the original conditions. The pressure of the carbon dioxide therefore increases as the temperature rises.

Had the dissociation occurred with evolution of heat, then the opposite effect would be observed. Hydrogen iodide dissociates to a smaller and smaller extent as the temperature rises, and from this point of view endothermic substances must be regarded as increasing in stability with rise in temperature.

CHAPTER XXXIX.

Chemical Equilibrium in Aqueous Solution.

Many reactions which occur in aqueous solution are reversible, and the direction in which any reaction proceeds, as well as the condition of equilibrium, then depends, as in other cases, on the relative molecular concentrations of the substances concerned in it. When, for example, nitric acid is added to an aqueous solution of sodium chloride and the solution is evaporated, the residue consists of a mixture of sodium chloride and sodium nitrate; when this residue is dissolved in water, and again evaporated with nitric acid, and these operations are repeated several times, crystals of pure sodium nitrate are ultimately deposited.

On the other hand, when a solution of sodium nitrate is repeatedly evaporated with hydrochloric acid in the manner just described, a residue of pure sodium chloride is finally obtained.

These facts show that the reactions,

$$NaCl + HNO_3 \longleftrightarrow NaNO_3 + HCl,$$

are reversible, and the results in the above two cases are in accordance with the general principle already explained.

On aqueous solutions of sodium chloride and nitric acid being mixed together, the reaction proceeds from left to right until a condition of equilibrium is attained; on evaporating, the volatile nitric and hydrochloric acids pass away, and there remains a mixture of the two salts. On nitric acid being again added, a further quantity of sodium chloride is converted into nitrate and a new equilibrium is reached; on evaporating, a further quantity of hydrochloric acid volatilises and sodium nitrate is deposited. Finally the change is complete, and the more rapidly, the greater the relative concentration of the nitric acid in each operation. For exactly similar reasons sodium nitrate is changed into sodium chloride when it is repeatedly evaporated with hydrochloric acid.*

This example illustrates the fact that the complete change of one salt into another by the action of an acid, that is to say, the complete displacement of one acid by another, depends on the removal from the system of the acid which is being displaced, or of the salt which is being formed.

For this reason nearly all acids decompose carbonates. The carbonic acid which is first produced by a reversible double decomposition,

$$Na_2CO_3 + 2HCl \longleftrightarrow 2NaCl + H_2CO_3,$$

decomposes into carbonic anhydride, which escapes as a gas, and water; the reverse action, namely, the decomposition of sodium chloride by carbonic acid, is thus almost entirely prevented, so that the reaction proceeds continuously in the one direction. The liberation of carbon dioxide from a carbonate is therefore used as a test for an acid.

Sulphuric acid is far less readily volatile than nitric acid or hydrochloric acid; hence sodium nitrate and sodium chloride are decomposed completely when they are heated with excess of sulphuric acid, because the removal of the volatile acid prevents the occurrence of the reverse reaction. Sodium chloride or sodium nitrate cannot be obtained by evaporating sodium sulphate with hydrochloric or with nitric acid; although in aqueous solution the reversible action,

$$Na_2SO_4 + HCl \longleftrightarrow NaCl + NaHSO_4,$$

occurs, the hydrochloric acid volatilises on the solution being evaporated, and the reaction proceeds from right to left until the whole of the sodium chloride is decomposed. Sodium silicate, however, may be obtained by strongly heating sodium sulphate with silica (p. 292),

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* The fact that hydrochloric and nitric acids decompose one another (p. 236) may be left out of consideration, as this decomposition makes no essential difference to the argument.

$$Na_2SO_4 + SiO_2 \longleftrightarrow Na_2SiO_3 + SO_3,$$

because sulphur trioxide is volatile, while silica is not.

The liberation of ammonia from its salts (p. 268) by the action of calcium hydroxide or sodium hydroxide depends on this same general principle. The reactions,

$$2NH_4Cl + Ca(OH)_2 \longleftrightarrow CaCl_2 + 2NH_4(OH)$$
$$\text{and} \quad NH_4Cl + NaOH \longleftrightarrow NaCl + NH_4(OH),$$

are reversible in aqueous solution, but as ammonium hydroxide decomposes readily, giving ammonia, which escapes, and water, on an ammonium salt being heated with excess of a fixed alkali (p. 268) the reaction proceeds from left to right until the whole of the salt is decomposed.

The complete decomposition of a chloride when its aqueous solution is treated with excess of silver nitrate (p. 149), and the complete decomposition of a sulphate when its aqueous solution is treated with barium chloride (p. 227), offer further illustrations of this general principle. In these reactions,

$$NaCl + AgNO_3 = NaNO_3 + AgCl$$
$$Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4,$$

one of the products is *insoluble* in the liquid present, and when it separates in the *solid* state the result is essentially the same as if it had been removed altogether, as its molecular concentration is practically *nil*. Hence in all cases in which an insoluble product is formed from two soluble substances, the reaction proceeds practically to completion.

Although barium sulphate is almost insoluble in water, it is slowly converted into barium carbonate when it is heated with a large quantity of a concentrated aqueous solution of sodium carbonate,

$$BaSO_4 + Na_2CO_3 \longleftrightarrow BaCO_3 + Na_2SO_4.$$

This is due partly to the fact that one of the products, namely, the barium carbonate, is even less soluble than the sulphate, and consequently, although the latter is only slowly attacked, the change from right to left takes place still more slowly; also to the fact that the concentration of the sodium carbonate always greatly exceeds that of the sodium sulphate.

HYDROLYSIS.

There are so many chemical changes in which water plays a part that the term **hydrolysis** is used to denote any reaction in which water undergoes double decomposition (p. 147); as a result of such changes the water molecules are resolved into hydrogen atoms and hydroxyl-groups (p. 250), and these portions of the water molecules are both fixed in the *products of hydrolysis.*

When, for example, phosphorus trichloride (p. 543) is treated with water it is *hydrolysed*, or undergoes hydrolysis; each of the three chlorine atoms is displaced by a univalent hydroxyl-group (–OH), hydrogen chloride and phosphorous acid being formed as products of hydrolysis,

$$PCl_3 + 3H_2O = 3HCl + P(OH)_3.$$

The decomposition of water by an element, such as sodium (p. 253), is not a process of hydrolysis, but the term *might* be applied to the combination of an anhydride or of a basic oxide with water, as the elements of water are fixed in the product.

Some hydrolyses are not appreciably reversible reactions, as, for example, that given above, but many are reversible; in the latter case the direction in which the reaction proceeds and the condition of equilibrium depend on the relative molecular concentrations of the substances taking part in the change.

Thus when bismuth trichloride (p. 570) or antimony trichloride (p. 564) is treated with water hydrolysis occurs, and in each case two atoms of chlorine are displaced by hydroxyl-groups,

$$BiCl_3 + 2H_2O \longleftrightarrow 2HCl + BiCl(OH)_2$$
$$SbCl_3 + 2H_2O \longleftrightarrow 2HCl + SbCl(OH)_2.$$

The primary product of hydrolysis in both cases is unstable, and decomposes, giving a precipitate of bismuth oxychloride or of antimony oxychloride as the case may be,

$$\mathrm{BiCl(OH)_2 = BiOCl + H_2O}$$
$$\mathrm{SbCl(OH)_2 = SbOCl + H_2O.}$$

As these secondary products are insoluble in water, hydrolysis is practically complete in presence of a large excess of water; but if hydrochloric acid is added in excess, the precipitated oxychlorides are reconverted into the trichlorides,

$$\mathrm{BiOCl + 2HCl = BiCl_3 + H_2O,}$$

and the hydrolysis of the trichlorides is prevented by the increased concentration of the hydrochloric acid. Consequently both the trichlorides dissolve in concentrated hydrochloric acid without undergoing hydrolysis.

Many other salts are hydrolysed by water. In some, as in the above cases, an insoluble product is formed, and consequently when excess of water is used the change is practically complete. But in others, in which the products of hydrolysis are soluble, the change, which is of course incomplete, can only be detected by examining the solution in some appropriate manner.

Many carbon compounds offer excellent illustrations of the phenomenon of hydrolysis.

The Law of Mass Action.—The idea of chemical equilibrium was first brought forward by Berthollet (1799), who also recognised the fact that the condition of equilibrium depends on the *relative concentrations* of the substances taking part in it. The law relating to such phenomena was first clearly formulated by Guldberg and Waage (1867) and is known as the **law of mass action**; as it was based on a study of *reversible double decompositions*, it may be explained by considering a reaction of this type.

When two substances, A and B, are transformed by double decomposition (or double substitution) into two new substances, A′ and B′, and under the same conditions, A′ and B′ can transform themselves into A and B, neither change is complete. At the end of the reaction the four substances, A, B, A′, B′, are all present.

When equilibrium is attained the speed of formation of A′ and B′ is equal to that of the formation of A and B, because the two reactions are proceeding with equal velocity. At any constant temperature the reaction velocity depends on (1) the *velocity coefficient* of the reaction, which is determined by the nature of the substances concerned; (2) the *active masses* of the substances A and B, or A′ and B′, that is to say, their *concentrations* as measured by the number of gram-molecules in one litre of the mixture.*

Now it was shown by Guldberg and Waage that the reaction velocity is proportional to the *product* of the active masses of the two interacting substances, A and B, or A′ and B′. If then the velocity coefficient of the direct reaction is k, and the molecular concentrations of A and B are c_1 and c_2 respectively, the velocity (v) of this reaction is $v = kc_1c_2$. Similarly, if the velocity coefficient of the reverse reaction is k', and the molecular concentrations of A′ and B′ are c_1' and c_2' respectively, then the velocity (v') of this reaction is $v' = k'c_1'c_2'$. At any moment the total speed of formation of A′ and B′ is given by the difference between the speed at which they are being formed from A and B and the speed at which they are changing into the original substances A and B; this difference is represented by $v - v' = kc_1c_2 - k'c_1'c_2'$.

At equilibrium the total speed of the reaction is 0, the direct and opposed reactions having equal velocities, so that here

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* The term active mass or molecular concentration is only used in reference to the number of molecules of a substance in the gaseous, liquid, or dissolved state; the active mass of a *solid* may be taken as constant as regards its influence on the equilibrium, because the concentration of a solid in a solution, or of the gases it gives off, is constant at equilibrium at any fixed temperature, and it is on the dissolved, gaseous, or liquid substance that the velocity depends.

$$kc_1c_2 - k'c_1'c_2' = 0, \text{ or } \frac{k}{k'} = \frac{c_1'c_2'}{c_1c_2},$$

and since k and k' are constant for any given temperature, then $\frac{k}{k'}$, and therefore $\frac{c_1'c_2'}{c_1c_2}$ is also constant, no matter what were the quantities of A, B, A′ and B′ originally present.

This value $\frac{k}{k'}$ (usually represented by K) is called the *equilibrium constant* of the reversible reaction, and may be determined experimentally by ascertaining the composition of the mixture, that is to say, the values of c_1, c_2, c_1', c_2' at the condition of equilibrium.

The foregoing discussion deals with the simple case in which only one molecule of each of the reacting constituents takes part in the direct and opposed reactions. When the equation representing the reactions involves more than one molecule of each of the reacting constituents, say n_1, n_2, and n_1' and n_2',

$$n_1\text{A} + n_2\text{B} = n_1'\text{A}' + n_2'\text{B}',$$

then the velocities are to be represented as

$$v = kc_1^{n_1}c_2^{n_2} \text{ and } v' = k'c_1'^{n_1'}c_2'^{n_2'},$$

and at equilibrium

$$\text{K} = \frac{k}{k'} = \frac{c_1'^{n_1'}c_2'^{n_2'}}{c_1^{n_1}c_2^{n_2}},$$

and this law applies as strictly to those reactions which occur instantaneously as to those which proceed with measurable speed.

The application of the law of Guldberg and Waage to one or two cases already dealt with may be pointed out. In the equations which are used, the concentrations of the reacting molecules are indicated by letters underneath the respective formulæ.

(*a*) The dissociation of calcium carbonate,

$$CaCO_3 = CaO + CO_2$$

Here $\frac{k}{k'} = K = \frac{c_2 c_3}{c_1}$, but, as $CaCO_3$ and CaO are solids, their active masses c_1 and c_2 are constant at any given temperature; hence the equilibrium equation may be written,

$$K = c_3;$$

or the concentration of the carbon dioxide above a mixture of lime and calcium carbonate is constant at equilibrium; hence its pressure, too, is constant for any given temperature.* In cases of dissociation K is known as the **'dissociation constant.'**

(*b*) The equilibrium between Fe, Fe_3O_4, H_2O, and H_2,

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Here $K = \frac{c_3 c_4^4}{c_1 c_2^4}$; but as c_3 and c_1 are constants, Fe and Fe_3O_4 being solids, it follows that $\frac{c_4^4}{c_2^4}$, and therefore $\frac{c_4}{c_2}$ is constant. In other words, at equilibrium the ratio of the concentrations of the steam and the hydrogen is always the same at any given temperature.

(*c*) The dissociation of nitrogen tetroxide,

$$\underset{c_1}{N_2O_4} = \underset{c_2}{NO_2} + \underset{c_2}{NO_2}$$

Here $K = \frac{c_2^2}{c_1}$ at a fixed temperature. The ratio of c_2 to c_1 is not fixed, but depends on the absolute concentrations of the gases; in other words, it varies as the mixed gas is more or less compressed.

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* This is argument in a circle, certainly. The case is used, however, only to show that the conclusions arrived at are consistent with the facts.

(*d*) The dissociation of hydrogen iodide,

$$\underset{c_1}{HI} + \underset{c_1}{HI} = \underset{c_2}{H_2} + \underset{c_3}{I_2}$$

Here $K = \frac{c_2 c_3}{c_1^2}$. Starting with pure hydrogen iodide or with equimolecular proportions of hydrogen and iodine, then $c_2 = c_3$, and $K = \frac{c_2^2}{c_1^2}$, so that $\frac{c_2}{c_1}$ is also constant. In other words, the ratio of hydrogen to hydrogen iodide is constant at constant temperature, and therefore compression, expansion, or dilution with an *inert* gas does not affect the proportion of the gas which is dissociated. This is true in all instances where the number of gaseous or dissolved molecules on each side of the chemical equation is the same.

An increase in the hydrogen concentration, other things being equal, will of course result in an increase in the concentration of the hydrogen iodide at the expense of the free iodine vapour. That is, the amount of dissociation is decreased in presence of excess of one of the products of dissociation.

Hence it is that many substances which have an 'abnormal' vapour density (footnote, p. 370) owing to the occurrence of dissociation give a nearly normal value when vaporised in an atmosphere of either of the products of their dissociation.

(*e*) The dissociation of phosphorus pentachloride,

$$PCl_5 = PCl_3 + Cl_2$$

Here $K = \frac{c_2 c_3}{c_1}$ or $\frac{c_1}{c_2} = \frac{1}{K}c_3$, or the ratio of undissociated phosphorus pentachloride to phosphorus trichloride is proportional to the concentration of the free chlorine. Similarly $\frac{c_1}{c_3} = \frac{1}{K}c_2$, or the ratio of undissociated pentachloride to free chlorine is proportional to the free trichloride. Hence nearly normal vapour densities are obtained on vaporising phosphorus pentachloride in an atmosphere of either chlorine or of phosphorus trichloride.

CHAPTER XL.

Osmotic Pressure.

When a glass vessel filled with spirits of wine is closed with a bladder and the whole is then immersed in water, the bladder expands, indicating an increase in the contents of the vessel, and may burst as the result of the increase of internal pressure. Further, when two different liquids, such as water and a solution of a salt, are separated by an animal membrane, there results a change in level, the salt solution increasing in quantity at the expense of the water.

In these experiments the water passes freely through the animal membrane, but the dissolved substance does not, except to an inappreciable extent.

Any partition, such as animal membrane, through which some substances, but not others, can pass, is termed a *semi-permeable* partition or diaphragm. Various semi-permeable partitions much more efficient than animal membrane can be prepared.

When a drop of a concentrated solution of potassium ferrocyanide (p. 705) is carefully placed in a very dilute solution of copper sulphate, the drop is immediately surrounded by a coherent film of insoluble copper ferrocyanide, which is formed by double decomposition. This film is a semi-permeable partition; it is impervious to the two salts from which it has been produced, but water from the external dilute solution passes through it freely, and there soon results a *pressure* which causes the film to burst. The liquid emerging at once forms a new film, which in the course of time bursts, and by a continuation of these processes a branched mass of considerable size is ultimately formed.

In order to measure the *pressure* in cases of this kind the semi-permeable film must be artificially supported; this is accomplished by producing the film or partition in the walls of a clean, porous earthenware pot or 'cell.'

The cell is first soaked for some hours in a dilute solution of copper sulphate; it is then washed out with water, filled with a dilute solution of potassium ferrocyanide, and allowed to stand in a solution of copper sulphate. In this way a semi-permeable partition of copper ferrocyanide is formed within the porous earthenware.

If various solutions are successively placed in such a cell and the mouth is closed with a perforated rubber stopper so that the interior may be connected with a pressure-gauge (or manometer), then on placing the cell in water the increase in pressure which is observed may be measured.

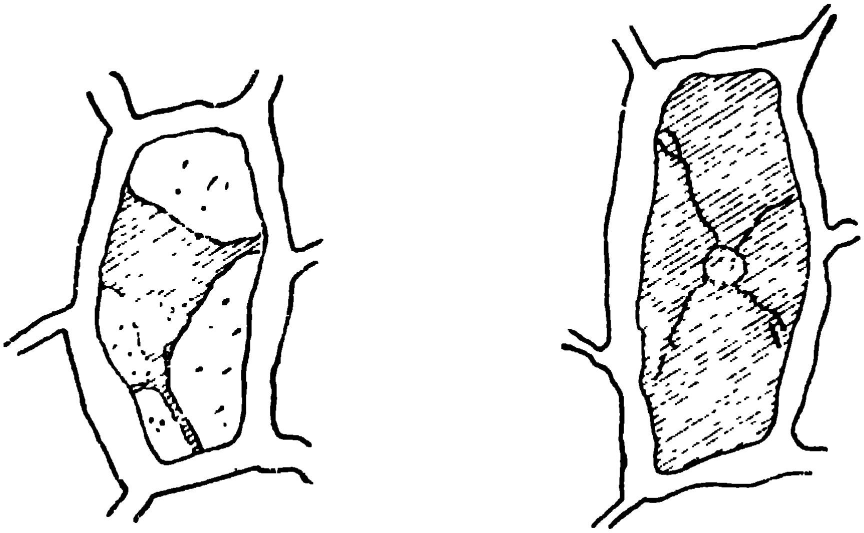

Fig. 90.

This pressure is called **osmotic pressure**, and the values for the osmotic pressures of solutions are strikingly large. Thus even with 1 per cent. solutions, osmotic pressures of two or three atmospheres are obtained with salts and other electrolytes, and pressures of more than half an atmosphere with cane-sugar, but only small pressures are given by solutions of certain amorphous materials, such as gums.

Aqueous solutions which produce the same osmotic pressure are called *isotonic*, and all such solutions, when separated from one another by a semi-permeable membrane, are in equilibrium with one another.

Methods for determining whether or not solutions are isotonic have been devised, and among the more interesting is that based on the observation that when living cells are placed in strong salt solutions, the protoplasmic contents appear to withdraw from the side of the cell (plasmolysis), as shown in fig. 90.

The reason appears to be that the protoplasm is covered by a embrane which resembles those formed by precipitation and is pervious to water but impervious to most dissolved substances. The contents of this membrane contain dissolved substances, and if placed in salt solutions of high concentrations they lose water and contract, while in more dilute solutions their tendency would rather be to expand. Solutions of substances soluble in water may be made and diluted with known quantities of water until they just cause plasmolysis with similar cells; these are then nearly isotonic' with the cell contents, and therefore with one another. Blood cells, as well as plant cells, may be used.

Osmotic pressure increases with temperature, and is proportional to the absolute temperature; hence solutions which are isotonic at low, are also isotonic at higher, temperatures.

The osmotic pressure of any solution is proportional to the weight of dissolved substance in a given volume of the solution; further, quantities of different dissolved substances, which are in the ratio of the molecular weights of these substances, produce equal pressures at equal temperatures.

The molecular weight of a dissolved substance may therefore be determined by measuring the osmotic pressure of a solution containing a known weight of that substance, and comparing the value with that obtained at the same temperature with a solution of a given weight of some substance of known molecular weight.

The measurement of osmotic pressure, however, presents considerable difficulty, and therefore this method of determining molecular weight is little used. Moreover, it is much easier to determine other values which are proportional to osmotic pressure, such as the depression of the freezing-point, or the elevation of the boiling-point.

The most important theoretical result of a study of osmotic pressure is that the osmotic pressure of a substance is the same as the gas pressure which it would exert if it existed as a gas in the same volume at the same temperature in absence of the solvent (**van't Hoff's Law**). In other words, the laws of Boyle (p. 154) and of Gay-Lussac or Charles (p. 158), and Avogadro's hypothesis (p. 193), apply to dissolved substances if osmotic pressure is used instead of gas pressure. Thus a 1 per cent. solution of cane-sugar (M.W. 342) contains 224 grams or $\frac{224}{342} = 0{\cdot}65$ gram-molecules in 22·4 litres, so that at normal temperature it exerts an osmotic pressure of 0·65 of an atmosphere.

CHAPTER XLI.

The Determination of Molecular Weight.

In some of the cases of dissociation which have just been considered, and in others which will be referred to later, the principal or the only evidence of the occurrence of dissociation is afforded by vapour density determinations.* The results of these determinations show that the vapour density varies with the temperature, which would *not* be the case if the number of molecules in the vapour remained constant, or, in other words, if the molecular weight of the substance underwent no change. The great importance of a knowledge of molecular weight has already been pointed out, and the methods used in determining the vapour density, and therefore also the molecular weight, in the case of a gas or a readily volatile liquid or solid have been described (pp. 159, 160).* It is obvious, however, that these particular methods are limited in their application, and could not be conveniently used in the case of substances of high boiling-point, or of those which decompose without vaporising.

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* Substances which dissociate are still sometimes spoken of as having *abnormal* vapour densities, because when their densities were first examined, and before the occurrence of dissociation had been recognised, the values obtained experimentally differed from those which were calculated from the known (or probable) molecular formulæ, and therefore seemed to be abnormal.

Fortunately other ways of determining molecular weight, applicable in such instances, are known.

VICTOR MEYER'S METHOD FOR THE DETERMINATION OF VAPOUR DENSITY.

When a substance vaporises, but does so only at a relatively high temperature, its vapour density (and from this the molecular weight) is determined by a method devised by Victor Meyer.

The principle of this method is to convert a *weighed quantity* of the substance into vapour very rapidly, and in such a way that the vapour displaces its own volume of air; the *volume* of the displaced air, which is equal to that of the vapour under any conditions of temperature and pressure common to both, is then measured.

The apparatus is shown in fig. 91. The bulb tube (*a*, *b*) is closed (at *a*) by means of a rubber stopper, and is heated by the vapour of some liquid of constant boiling-point † contained in the outer vessel (*c*); as the air expands it escapes through the narrow tube (*d*), which dips under the water in the vessel (*e*). As soon as the temperature of the bulb tube (*a*, *b*) becomes constant—that is to say, when bubbles of air cease to escape from (*d*)—the graduated tube (*g*) is filled with water and inverted over the end of (*d*); the stopper (*a*) is now removed, and a small bottle or bulb completely filled with a weighed quantity (about 0·05 gram) of the liquid is dropped into the apparatus,* the stopper (a) being replaced as quickly as possible. The substance immediately vaporises, and the vapour forces some of the air out of the apparatus into the graduated vessel (g). When air ceases to issue from (d), the stopper (a) is at once taken out to prevent the water in (e) from being sucked back into the apparatus.

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* The method given there (p 160) for use in the case of readily volatile substances is known as *Dumas' method*.

† In determining the vapour density of substances of high boiling-point, diphenylamine (b.p. 310°) or sulphur (b.p. 448°) may be used, or the bulb tube (*ab*) may be heated at a constant temperature in a metal bath.

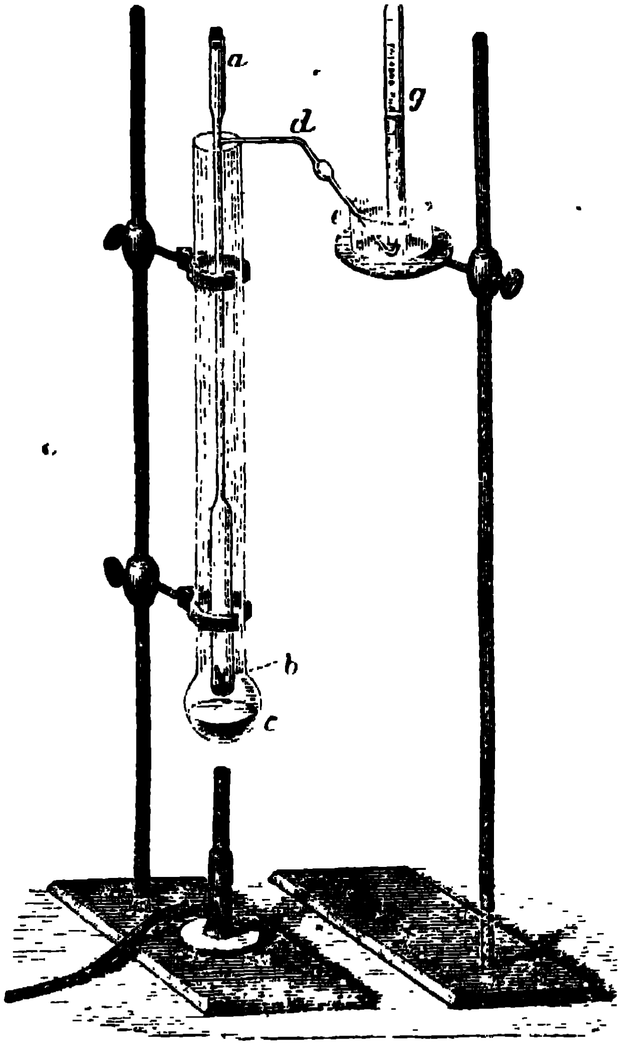

Fig. 91.

The *volume* of the vapour is ascertained by measuring the volume (v) of the air in the graduated tube, its *temperature* (t) and the barometric *pressure* (B) being noted. The volume of the air in (g) is not the same as that actually occupied by the hot vapour in (a, b), because the displaced air has been cooled, and is measured under a different pressure. Its volume now is *equal to that which the given weight of vapour would occupy under the same conditions of temperature and pressure.*

The temperature of the volume, v, of air being t°, and the height of the barometer B, the volume at N.T.P. would be $v \times \frac{273}{273+t} \times \frac{B-T}{760}$, T being the tension of aqueous vapour at $t°$ (p. 156). The weight of an equal volume of hydrogen at N.T.P. is then calculated and divided into the weight of the substance taken; the vapour density is thus obtained, and from it the molecular weight (compare p. 204).

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* In order to prevent fracture, a little dry asbestos, glass-wool, or sand is placed in (b).

The liquid in (*c*) should have a boiling-point at least 25° higher than that of the substance of which the vapour density is required in order that the latter may be *rapidly* vaporised—otherwise its vapour may condense again higher up the tube. If, as is generally the case, the temperature of the air in the tube (*a*, *b*) is lower at the top than at the bottom, this is of no consequence; nor does it matter if the displaced air is colder than the vapour, or if the vapour is cooled a *little* while it is displacing the air. This is because any diminution in the volume of the air displaced from the tube (*a*, *b*) arising from these causes is exactly compensated for during the subsequent cooling to $t°$; the lower the original temperature, the smaller the subsequent contraction. If, for example, the hot vapour measured 25 c.c. at 250°, but only displaced 24·04 c.c. of air owing to the latter being of the average temperature of 230°, the 24·04 c.c. of air at 230° would occupy the same volume as 25 c.c. at 250° if both were cooled to t.

HOFMANN'S METHOD FOR THE DETERMINATION OF VAPOUR DENSITY.

The principle of this process is to convert a *weighed quantity* of substance into vapour in the Torricellian vacuum (footnote, p. 17), and then to measure the *volume* of the vapour under known conditions of temperature and pressure. A graduated barometer tube (*a*, *b*, fig. 92), about 85 cm. long and 35 mm. wide, filled with and then inverted in mercury, is surrounded by a wider tube (*c*), through which the vapour of some liquid boiling at a known and constant temperature is passed.* For this purpose the upper end of the outer tube

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* The liquids commonly employed are water (b.p. 100°), xylene (b.p. 140°), aniline (b.p. 183°), and ethyl benzoate (b.p. 213°).

(*c*) is connected with a vessel (*d*), usually made of copper, containing the heating liquid, which is kept in rapid ebullition. The condensed liquid escapes through the side-tube (*e*).

As soon as the barometer tube is at a constant temperature, a weighed quantity (about 0·05 gram) of the substance contained in a small stoppered vessel, which it fills completely, is placed under the open end (*b*). The vessel immediately rises to the surface of the mercury in the tube, the stopper is blown out, the substance vaporises into the Torricellian vacuum, and the mercury is forced downwards; as soon as the level remains stationary, the *volume* of the vapour is noted. The *temperature* of the vapour is the boiling point of the liquid employed to heat the barometer tube. The *pressure* is determined by subtracting the height of the column of mercury in the inner tube (*a*, *b*), above the level in the trough, from the height of the barometer, both readings having been first reduced to 0°.* The *weight* of the vapour is that of the substance taken.

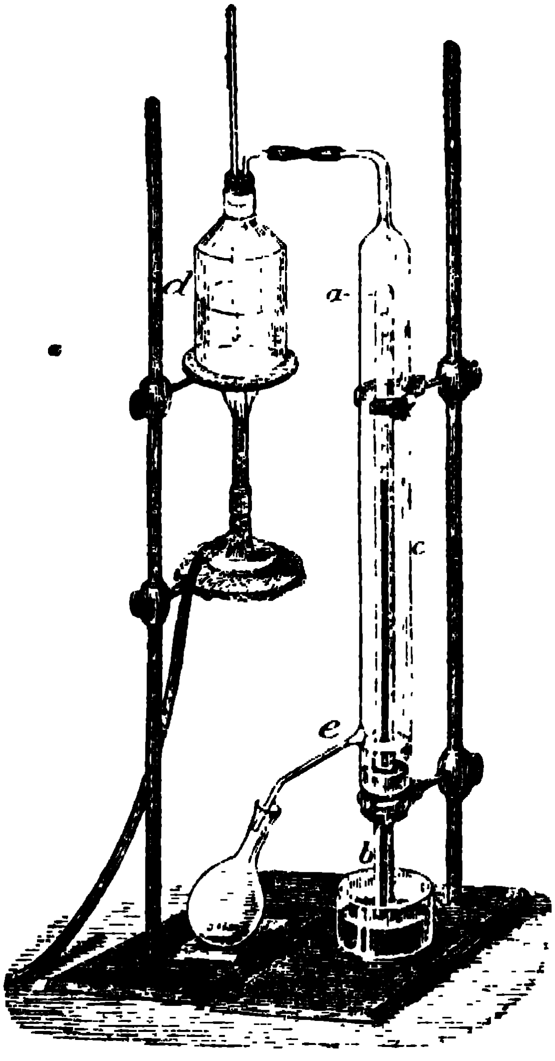

Fig. 92.

The great advantage of this method lies in the fact that it affords a means of determining the vapour density of substances under greatly *reduced pressures*, and therefore at temperatures very much below their ordinary boiling-points; hence it is often possible to determine the vapour density of a substance which would decompose if it were heated under atmospheric pressure.

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* For this purpose a correction must be made for the expansion of the mercury.

DETERMINATION OF MOLECULAR WEIGHT BY THE CRYOSCOPIC METHOD.

For ascertaining the molecular weight of a substance which cannot be vaporised several methods may be used. The first of these to be described is based on a determination of the lowering of the freezing-point of a solvent in which the given substance is dissolved.

It has already been stated (p. 313) that when a dilute aqueous solution of salt is cooled, crystals of pure ice begin to separate at some temperature *below* the freezing-point of water: that is to say, the freezing-point of water is lowered or depressed by the presence of the dissolved saline matter. Other substances, such as sugar, sulphuric acid, sodium hydroxide, &c., also depress the freezing-point of water, and in general the freezing-point of any liquid (water, acetic acid, p. 277; benzene, p. 125, &c.) is depressed by matter in solution.*

Now it was proved experimentally by Raoult that the extent to which the freezing-point of a solvent is lowered is directly proportional to the weight of the substance dissolved in a given weight of the solvent; that is to say, the depression is proportional to the concentration of the solution. Thus a 1 per cent. solution of cane-sugar freezes at −0·058°, a 2 per cent. solution at −0·116°, a 3 per cent. solution at −0·174°, and so on. The depression produced by a given substance, therefore, is proportional to the number of molecules of that substance in a given weight of the solvent.

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* If ice and an aqueous solution are in equilibrium at a certain temperature and atmospheric pressure, and more of the dissolved substance is added to the solution, then, in accordance with Le Chatelier's rule (p. 356), ice will melt in order to neutralise, as far as possible, the change in the concentration of the solution, which it does by adding to the amount of water present. In doing so, however, it will absorb heat, and finally a new state of equilibrium will be obtained, with a lower temperature. The temperature at which ice is in equilibrium with the solution is, however, the 'freezing-point of the solution;' hence the presence of a dissolved substance in a liquid must depress its freezing-point.

It was also proved that *equal numbers of molecules of different substances dissolved in a given weight of a given solvent produce the same depression of the freezing-point;* hence the depression is independent of the *nature* of the molecules. The molecular weights of cane-sugar, glucose, and acetone,* for example, are 342, 180, and 58 respectively; if, then, three solutions are made by dissolving 3·42, 1·8, and 0·58 grams respectively of these substances in, say, 100 grams of water, the three solutions contain molecular proportions, or equal numbers of molecules, of the dissolved substances, and their freezing-points are identical

The above statements are true only in the case of dilute (up to, say, 5 per cent.) solutions, but by finding experimentally the freezing-point of a very dilute solution of *known* concentration, the depression which should be caused by dissolving 1 gram-molecule of the substance in 100 grams of the solvent can be calculated by simple proportion; the value thus obtained is called the **molecular depression,** and is a *constant* (K) for a given solvent. Thus, since 0·54 gram of glucose depresses the freezing-point of 12 grams of water 0·475°, and the molecular weight of glucose is 180, 1 gram-molecule of glucose dissolved in 100 grams of water should give a molecular depression (K) of 19°.

0·54 g. of glucose in 12 g. of water corresponds with 4·5 g. of glucose in 100 g. of water, and 4·5 : 180 : : 0·475° : 19°. The molecular depression, then, **of water,** is 19°.

The molecular depression, K, of any solvent having been determined experimentally with the aid of substances of

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* The reason for choosing these substances as examples instead of some commoner compounds, such as salt or blue vitriol, will appear later (p. 386).

known molecular weight, it is then possible to determine the molecular weight of any other substance which is soluble in that solvent by finding the depression, D, produced by a known weight of the substance dissolved in a known weight of the solvent.

Thus if 0·42 g. of a substance dissolved in 10 grams of water gives a depression D = 0·63, then since 100 g. of the solvent contain 4·2 g. of substance, and D : K . : 4·2 : M.W., the molecular weight is $= \frac{19 \times 4 \cdot 2}{0 \cdot 63} = 127$

Now many different solvents may be used for such experiments, and since most substances are soluble in some liquid, it is possible to determine the molecular weights of a great many substances by the method here described, which is known as the **cryoscopic method.** This is a fact of great importance, because the determination of molecular weight from vapour density is only possible in the case of those substances which are volatile. The results obtained by the cryoscopic method are only approximately correct, but this is a matter of no importance for reasons already given in dealing with the results of vapour density determinations (p. 204).

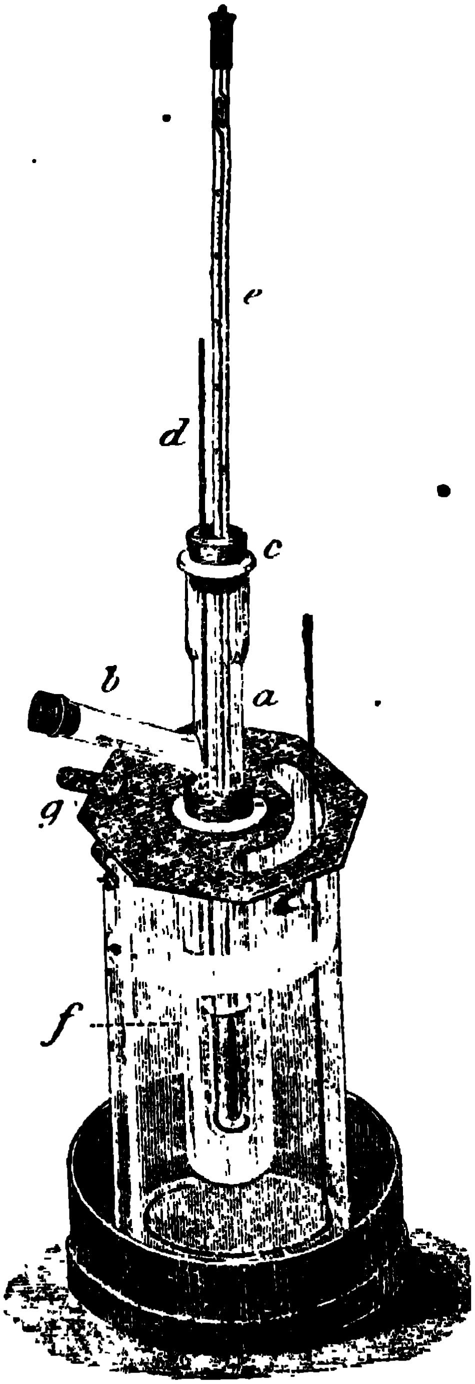

Fig. 93.

The apparatus generally used in determining molecular weights by the cryoscopic method was devised by Beckmann, and is shown in fig. 93. A large tube (*a*), about 3 cm. in diameter, and provided with a side-tube (*b*), is closed with a cork (*c*), through which pass a stirrer (*d*), and a thermometer (*e*) graduated to $\frac{1}{100}°$. A weighed quantity (about 15 grams) of the solvent is placed in the tube (*a*), which is then fitted into a wider tube (*f*), which serves as an air-jacket and prevents a too rapid change in temperature. The apparatus is now introduced through a hole in the metal plate (*g*) into a vessel which is partly filled with a freezing mixture or some liquid, the temperature of which is about 5° lower than the freezing-point of the solvent. The solvent in (*a*) is now constantly stirred, whereon the thermometer rapidly falls, and sinks below the freezing point of the solvent, until the latter begins to freeze; the thermometer now rises again, but soon becomes stationary at a temperature which is the *freezing-point of the solvent.* A weighed quantity of the substance is now introduced through the side-tube (*b*), and after the solvent has been allowed to melt completely, the *freezing-point of the solution* is ascertained as before. The difference between the two freezing-points is the depression (D).

Fig. 94.

The *thermometer* used in such experiments has a very large bulb, and the total range shown on the scale is only about 6°, the smallest divisions corresponding with hundredths of a degree. The capillary tube connected with the bulb terminates above in a reservoir, as shown in fig. 94, and by warming the bulb very cautiously some of the mercury may be driven into this reservoir and detached from the main quantity by gently tapping the thermometer. It is thus possible to diminish the quantity of mercury in the bulb (and to increase it again when required), so that the top of the column in the capillary thread stands at some suitable point on the scale when the thermometer is at the temperature which is to be registered in the experiment. All that is required is that the thermometer shall show *differences* in temperature with a high degree of accuracy.

The constants (K) for some of the solvents frequently used are: water, 19; acetic acid, 39; benzene, 49.

DETERMINATION OF MOLECULAR WEIGHT BY THE EBULLIOSCOPIC METHOD.

Experiments have shown that the boiling-point of an aqueous solution of sugar, salt, or other substance is higher than that of water, and, in general, the boiling-point of a liquid is raised by the presence of dissolved non-volatile matter.* Further, experiments with *dilute* solutions of substances of known molecular weight have shown that (just as in the case of the *depression* of the freezing-point) the rise or *elevation* (E) of the boiling-point is directly proportional to the number of molecules of the substance contained in a given weight of a given solvent, but is independent of the nature of these molecules. From the results of such experiments the elevation which would be produced by dissolving 1 gram-molecule of a substance in 100 grams of the solvent may be calculated, and is found to be a constant (K) for the given solvent.

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* If a solution of sugar, salt, or other substance is in equilibrium with its vapour, within a closed vessel at a fixed temperature, and more of the soluble substance is added, the first result will be an increase in the concentration of the solution; in accordance with the rule (p. 356) a further change will then ensue, such as to neutralise this effect as far as possible. This can only occur by some of the vapour condensing and thus diluting the solution, a process which must entail a decrease in the pressure of the vapour. Were this experiment conducted at the boiling-point of the pure solvent - namely, the temperature at which the pressure of its vapour is equal to the atmospheric pressure – then on the addition of the soluble substance the vapour pressure would become less than before, and it would be necessary to raise the temperature in order to make the solution boil once more. Thus the presence of a dissolved substance in a liquid lowers its vapour-pressure and raises its boiling-point.

If, on the other hand, some of the dissolved substance is removed, the pressure of the vapour will increase until, when all the substance is removed, the boiling-point is equal to that of the pure solvent.

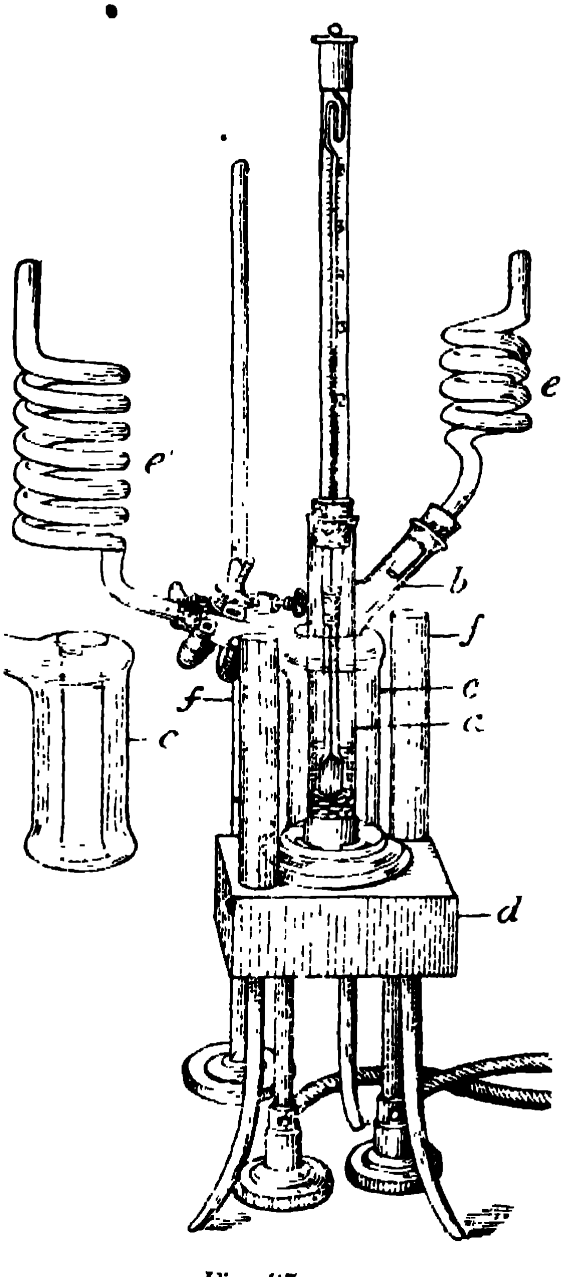

Fig. 95

It is thus possible to determine experimentally the molecular weight of any substance which is soluble in the given solvent by finding the elevation (E) which is produced by a known weight of the substance dissolved in a known weight of the solvent. E : K :: P : M.W., where P is the weight of substance dissolved in 100 g. of the solvent (compare p. 377).

A form of apparatus devised by Beckmann is shown in fig. 95. A known weight of the solvent is put into the tube (*a*), and after the thermometer is placed in position some glass beads are poured through the side-tube (*b*) until the bulb of the thermometer is nearly covered; the object of these beads is to ensure a regular boiling of the liquid. The tube (*a*) is surrounded by the outer jacket (*c*), which also contains some of the solvent; the object of this jacket is to prevent superheating. The apparatus is then placed, as shown, on an asbestos frame (*d*), and the condensers (*e*, *e′*) are fitted on. The asbestos frame, which is provided with chimneys (*f*, *f*), is then very gradually heated below, and when the solvent has been boiling constantly for some time (say thirty minutes), the position of the mercury thread is noted. The condenser (*e*) is now removed, and a weighed quantity of the substance (compressed into a tablet) is introduced through the side-tube, the condenser being immediately replaced. The temperature falls at first, but rapidly rises again, and in two or three minutes the position of the mercury thread becomes constant. The difference between the readings with the solvent and the solution respectively give the elevation E.

The constants for some common solvents are: water, 5·2; acetic acid, 25·3; benzene, 26·7; ether, 21·1. The results obtained with water are usually not very accurate, owing to the small value of the constant, and considerable experience is required before trustworthy results can be obtained with any solvent.

A simpler form of apparatus is that devised by Landsberger (fig. 96). A suitable quantity of the solvent is placed in the tube (*a*), which is about 16 cm. in height and 3 cm. in diameter, and which has a small opening at (*b*) for the escape of vapour; this tube (*a*) is fitted by means of a cork into a larger one (*c*), which serves as an air-jacket, and the outlet (*d*) of which is connected with an ordinary Liebig's condenser. The inner tube (*a*) is closed with a cork through which pass a thermometer graduated to $\frac{1}{20}$°, and a tube (*e*), the end of which has been cut off in a slanting direction, or perforated with a number of holes. The solvent in the tube (*a*) is not heated directly, but only by the vapour of the *same* solvent that is generated in the flask (*f*); in this way superheating is avoided.

The boiling point of the solvent alone is first determined by heating the solvent in the flask (*f*) and passing its vapour through the solvent in (*a*) until the thermometer shows a constant temperature; the solvent in (*a*) is then *mixed* with that in the flask (*f*), about the same quantity as was originally used being poured back into the tube (*a*). A weighed quantity of the substance is now placed in (a), and vapour from (f) is again passed until the temperature is again constant. The *difference* between the two readings gives the *elevation* E. The weight of the solvent in (a) at the time of the second reading has now to be found, and the molecular weight of the substance can then be calculated.

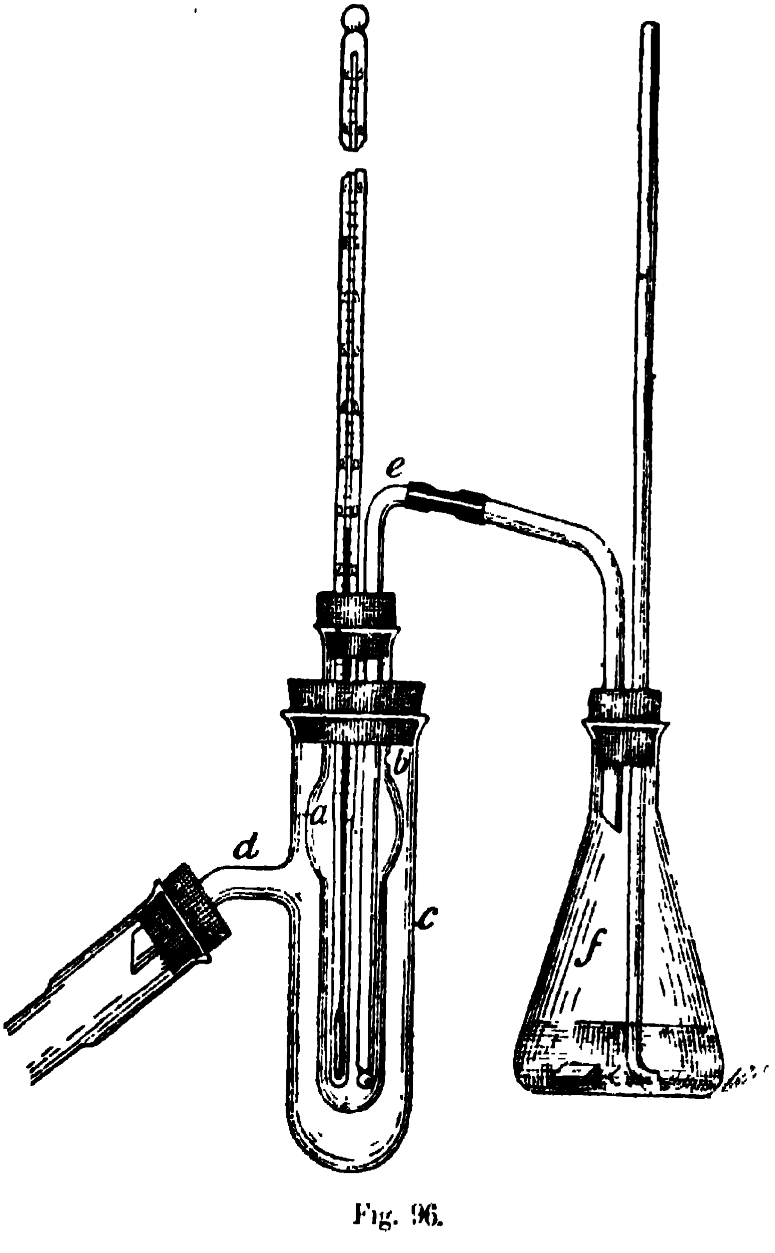

Fig. 96.

If the tube (a) is graduated, the weight of the solvent may be ascertained with sufficient accuracy by multiplying the volume by the specific gravity at the boiling point. The quantity of solvent originally placed in (a) should be so chosen that by the time the solvent is boiling constantly the total quantity amounts to about 10 grams.

SOME RESULTS OF MOLECULAR WEIGHT DETERMINATIONS.

By one or other of the methods which have now been described * it is possible to determine the molecular weights in the gaseous or in the dissolved state of a great number of the elements and their compounds; in fact, of any substance which vaporises below, say, 1000°, or which is appreciably soluble. By Victor Meyer's method the thermal dissociation of many substances is also established.

In the case of elements, it has been found that the molecules of different elements differ considerably in complexity. Those of mercury, for example, consist of single atoms, those of iodine of two, those of ozone of three, those of phosphorus of four, and those of sulphur of eight, atoms. The terms *monatomic*, *diatomic*, &c., are used to express the number of atoms in the molecule of an element. Ozone, for example, consists of triatomic, phosphorus of tetratomic, molecules. The fact that the molecules of an element may contain a considerable number of atoms is important in connection with allotropy, since the occurrence of the allotropic forms of oxygen is due to the existence of molecules of different complexity (p. 466), this may also be true in the case of other elements.

The results of molecular weight determinations by the vapour density method have also shown that in the case of a great many substances their molecules are more complex at low than at high temperatures, similarly, cryoscopic and ebullioscopic methods prove that the molecules of a given substance may be more complex in one solvent than in another, and more complex in concentrated than in dilute solutions. In the cases in question the complex molecules undergo dissociation, but this dissociation is similar to that studied in the case of nitrogen tetroxide in this, that the simpler molecules have the *same* percentage composition as the more complex ones; all such cases, therefore, may be represented by the equation $(M)_n \longleftrightarrow nM$, in which $(M)_n$ stands for *one* of the complex molecules.

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* Several other methods are known.

Now if there is any evidence that the simple molecules M are capable of an existence under other conditions, and that they retain their *structure* when they form the more complex molecules $(M)_n$, the formation of the latter is regarded as a process of aggregation or **association** rather than of chemical combination.

The compound hydrogen fluoride (p. 399), for example, is very closely related to hydrogen chloride, which is known to have the molecular formula HCl; for this and other reasons it may be concluded that hydrogen fluoride has the molecular formula HF. In accordance with this view, it is found that at temperatures above 88° the vapour density of hydrogen fluoride is 10, corresponding with the molecular formula HF (H = 1, F = 19). But at 30° the vapour density is 20, which corresponds with the molecular formula H_2F_2. Now if the molecular formula H_2F_2 were used, this formula would indicate that either fluorine or hydrogen has a greater valency than unity at the lower temperature, otherwise two H – F molecules could not unite; its use would also lead to the inference that the chemical properties of the compound so represented should be different from those of the compound HF, which exists at slightly higher temperatures. As, however, most of the properties and relationships of hydrogen fluoride are suitably expressed by the molecular formula HF, the more complex 'aggregates' which exist at ordinary temperatures are regarded as *associated molecules*.

A great many compounds show this phenomenon of association; but it is often extremely difficult to interpret the results of molecular weight determinations, and to decide whether the simpler or the more complex formula should be used to represent the molecule of the substance. Generally speaking, if considerations of valency point to the simpler formula and seem to preclude any change in the structure of the simpler molecules, then the existence of the more complex molecules is regarded as due to association.

A similar difficulty often arises as regards the representation of more or less stable substances which are formed from *different* molecules. Potassium fluoride, KF, for example, gives with hydrogen fluoride a crystalline substance which has the composition (KF + HF); and if the three elements in this substance are all univalent it is clear that the structures of the molecules H – F and K – F cannot have undergone any change. On this assumption, the substance may be regarded as consisting of the two different individual molecules HF and KF, and this may be indicated by writing its formula HF, KF. Such a compound is sometimes called a *molecular compound.*

The phenomenon of association and the formation of so-called molecular compounds provide further instances of the difficulty of distinguishing between a physical and a chemical change.

CHAPTER XLII.

The Ionic Dissociation Theory.

Although it can be shown experimentally that many salts are hydrolysed by water, most salts and most other substances, such as acids and basic hydroxides, which are soluble in water, *seem* to dissolve without undergoing chemical change (p. 328), and on their solutions being evaporated the original substances are recovered unchanged, or merely in a hydrated state. The fact that no *visible* sign of chemical change accompanies the process of solution does not of course prove that no such change occurs; when ammonium chloride is strongly heated it is completely decomposed into ammonia and hydrogen chloride, but no visible evidence of this fact is observed. Leaving out of account those cases in which it is known that a substance undergoes chemical change when it is placed in water—as, for example, the formation of hydroxides from anhydrides and from basic oxides, and the numerous instances of hydrolysis (p. 361)—the more general question whether or not the molecules of acids, basic hydroxides, and salts undergo change when they are dissolved in water has now to be studied. For this purpose it is necessary to consider in more detail some results of the examination of aqueous solutions.

When the molecular weight of an acid, basic hydroxide, or salt is determined by the cryoscopic or ebullioscopic method in *aqueous solution*, the value thus obtained is very much smaller than that calculated from the *known* molecular formula of the substance, and varies with the *concentration* of the solution. Thus the molecular weight of hydrogen chloride deduced cryoscopically is found to be *about* 25, whereas it is known from vapour density determinations that the molecular weight is really 36·5. Similarly, the molecular weight of sodium chloride is found to be *about* 35, whereas the true value cannot be less than 58·5, because the atomic weights of sodium and chlorine are 23 and 35·5 respectively.

In other words, 1 gram-molecule of an acid, basic hydroxide, or salt dissolved in 100 grams of water does not give the normal depression constant K = 19, which is obtained with cane-sugar, glucose, and other substances, but a much larger value; consequently the molecular weight deduced from the observed depression is much smaller than it is known to be.

Such observations seem to show that aqueous solutions of acids, basic hydroxides, and salts contain a larger number of molecules or particles than they would do had the acid, basic hydroxide, or salt dissolved unchanged, because the depression is directly proportional to the number of molecules or particles in the solution.

Now the fact that unexpected or 'abnormal' molecular weights are obtained by the cryoscopic or ebullioscopic method in the case of certain substances may be compared with the fact that 'abnormal' or unexpected molecular weights are sometimes obtained from vapour density determinations (p. 318); in the latter case the results are due to thermal dissociation, in consequence of which a given weight of substance gives rise to a larger number of molecules than it originally contains. It would seem, therefore, that the 'abnormal' depression of the freezing-point, leading to an 'abnormal' molecular weight, obtained with acids, basic hydroxides, and salts, must be due to some change whereby the number of molecules or particles contained in the undissolved substance has been increased during the process of solution.

This view is supported and can be best explained more fully by a reference to the phenomena of electrolysis (p. 300). Substances, such as cane-sugar, which give normal molecular weights in aqueous solution are all non-electrolytes. Acids, basic hydroxides, and salts which give lower molecular weights than the calculated values are all electrolytes (p. 301).

Now, as already stated (p. 305), the passage of an electric current through an aqueous solution of an electrolyte seems to be due to the presence in solution of oppositely charged particles or *ions*, which move through the solution to the electrodes, the positive ions (*cations*) being attracted to the negative electrode or cathode, the negative ions (*anions*) to the positive electrode or anode. An aqueous solution of sodium chloride, for example, behaves as if it contained positively charged particles of sodium and negatively charged particles of chlorine. Similarly, an aqueous solution of hydrogen chloride behaves as if it contained positively charged hydrogen ions and negatively charged chlorine ions.

But dry hydrogen chloride, whether gaseous or liquid, is a non-conductor of electricity, and under ordinary conditions is a very stable, strongly exothermic compound; water also, practically speaking, is a non-conductor (p. 467). And yet even a very feeble electric current can pass through a dilute aqueous solution of hydrogen chloride, and bring about the chemical decomposition of this compound. Similarly, many other stable substances which, when in a dry state, are non-conductors, give aqueous solutions which conduct the current, the dissolved substance undergoing chemical decomposition. Hence it seems that the mere process of dissolving an electrolyte in water prepares it in some way to transmit the current and to undergo chemical decomposition. If, then, it is assumed that during the process of solution the uncharged chemical molecules of the dissolving substance are resolved into oppositely charged particles, or ions, not only are the phenomena of electrolysis explained, but the unexpectedly low (or 'abnormal') molecular weights of electrolytes are also accounted for.

From these and other considerations, Arrhenius, in 1887, was led to put forward the theory of **ionic dissociation,** according to which the chemical molecules of electrolytes are dissociated into *ions* in aqueous solution to a greater or less extent. These ions may be single atoms or groups of atoms (radicles), but in either case every ion carries a definite charge of electricity, either positive or negative; as the original molecules are not charged, there are always both positive and negative ions produced from every dissociated molecule, and the total charges on the positive ions are equal and opposite to those on the negative ions.

During the electrolysis of acids, hydrogen is liberated at the negative electrode, whereas in the case of basic hydroxides and salts a metal is obtained as a *primary* product (p. 303) in place of hydrogen. It is concluded, therefore, that the ions of an *acid* are positively charged hydrogen atoms on the one hand, and negatively charged atoms or groups on the other; thus the ions of hydrochloric, nitric, and sulphuric acid are the charged atoms or radicles H, Cl; H, NO_3; and H, HSO_4 or 2 H, SO_4 respectively. In the case of basic hydroxides the positive ions are charged atoms of the metal or basic radicle (p. 266), and the negative ions are charged hydroxyl-groups; thus the ions of sodium and ammonium hydroxides are electrically charged Na, OH and NH_4, OH respectively. In the case of salts, the ions correspond with those of an acid, a charged metallic cation taking the place of the charged hydrogen ion; thus the ions of sodium chloride, sodium nitrate, and copper sulphate are the charged particles Na, Cl; Na, NO_3; and Cu, SO_4 respectively. Negative radicles such as NO_3, SO_4, and OH are not obtained as products of electrolysis, because they immediately react with the water present, or undergo chemical decomposition, when they are set free at the anode, giving rise to secondary products of electrolysis (p. 302).

Now Faraday's laws of electrolysis (p. 306) state that the same quantity of electricity is carried by the chemical equivalents of the different elements, and this is true of the various radicles which can act as ions. That is to say, the same charge or quantity of electricity is carried by two H ions as by two Na ions or by one Ca ion, and equal but opposite charges are carried by two Cl ions or by one SO_4 ion. If, then, it is assumed that all univalent ions carry a unit positive or negative charge, the number of unit charges carried by an ion is identical with its valency.

The unit positive charge of electricity is usually indicated by the sign $+$ or $^{\cdot}$, and the unit negative charge by $-$ or $'$.

Thus the following represent some of the more important ions:

Positive—$H^{\cdot}$, $Na^{\cdot}$, $NH_4^{\cdot}$, $Ba^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Fe^{\cdot\cdot}$ (ferrous), $Fe^{\cdot\cdot\cdot}$ (ferric).

Negative—OH', Cl', Br', I', NO_3', SO_4'', PO_4'''.

From this standpoint the ions of the elements differ altogether from the elements themselves, inasmuch as they possess electrical charges which alone must tend profoundly to alter their characters. In order that an ion may appear as an element, its electric charge must be removed, and this is what occurs during electrolysis. When the oppositely charged electrodes connected with a battery are immersed, for example, in a solution of an acid, the positively charged hydrogen ion is attracted to the negatively charged plate, and on coming into contact with it, gives up its charge, becoming an electrically neutral atom; two such discharged ions or atoms of hydrogen are now able to unite and form a molecule of free hydrogen. The hydrogen ions before discharge must exert a great mutual repulsion; but even if in spite of this they united they would not then constitute a hydrogen molecule, but a bivalent ion, $H_2^{\cdot\cdot}$.

The elements may thus be classed as *electro-positive* or *electro-negative* according to the behaviour of their compounds on electrolysis (p. 304). All those elements—namely, hydrogen and the metals—which are liberated at the negative electrode are electro-positive; this is one of the reasons why hydrogen may be considered to be a metal. All those elements, such as chlorine and the other halogens (p. 398), which are liberated at the positive electrode, and also those elements which are generally contained in the radicles liberated at the positive electrode, are electro-negative; oxygen, sulphur, and nitrogen, for example, are electro-negative. The terms electro-positive and electro-negative correspond, therefore, with the terms metal and non-metal respectively; but the classification based on the phenomena of electrolysis presents just as great a difficulty as that depending on other properties of the elements (p. 255).

When a compound which consists of more than two elements undergoes ionic dissociation, one of the ions is always a group of atoms, and a given element may sometimes be present in a positive, sometimes in a negative group. In the case of ammonium salts, for example, nitrogen is contained in the cation; whereas in nitrates it is present in the anion, and in ammonium nitrate it is present in both ions.

Similarly, many metals give rise to compounds which give anions of that metal; potassium permanganate, for example, gives the ions $K^{\cdot}$ and $MnO_4{}'$, and in this compound the manganese plays the part of an acid-forming or non-metallic element.

The fundamental conception in the ionic dissociation theory leads to the conjecture that as the electric current is carried through a solution of an electrolyte by the charged ions and not by the undissociated chemical molecules, the *conductivity* should depend on the extent of the ionic dissociation, and should be proportional for any given substance to the number of ions present. Now it has been found experimentally that, starting from a concentrated solution, the conductivity *of the matter in solution* increases as the solution is diluted until it reaches a maximum and constant value. It is, therefore, concluded that in the more concentrated solution ionic dissociation proceeds only until a condition of equilibrium is reached by reversible changes, such as those shown in the following equations:

$$HCl \longleftrightarrow H^{\cdot} + Cl'$$
$$NaOH \longleftrightarrow Na^{\cdot} + OH'$$
$$NaNO_3 \longleftrightarrow Na^{\cdot} + NO_3{}';$$

as the solution is diluted *ionisation* continues until it finally reaches a maximum which depends on the nature of the dissolved substance. The degree of ionic dissociation may be determined experimentally by measuring the conductivity of a solution of the substance and comparing the value with that of a solution of the same weight of substance in a very large quantity of water, the degree of dissociation may also be calculated from the results of cryoscopic and ebullioscopic experiments. It is thus found that electrolytes vary considerably as regards the extent to which they are ionised in solutions at equivalent concentration. Most salts, and especially those of the more electro-positive metals, exist mainly (about 80 per cent.) as ions in normal solution. The same is true of very *strong* acids such as hydrochloric and nitric acids, and of the *strong* alkaline hydroxides of the metals of the alkalis and alkaline earths. Sulphuric acid, on the other hand, is decidedly less fully ionised at the same equivalent concentration; while the very *weak* acids and bases are hardly ionised at all.

The *strength* of a solution of an acid or of a base is proportional to the number of hydrogen ions or hydroxyl ions respectively present; and, since dilution increases the degree of dissociation, all acids and all bases approach one another the more nearly in *strength* the more dilute the equivalent solutions in which they are contained.

It will be evident from the facts described in this chapter that the direct determination of the molecular weight of an electrolyte in aqueous solution is not possible, and that unless the electrolyte is volatile many things must be taken into account in deducing its molecular formula.

CHAPTER XLIII.

Some Applications of the Ionic Dissociation Theory.

REACTIONS BETWEEN IONS.

As a rule, reactions between ions proceed instantaneously, which is not generally the case with reactions between non-electrolytes; as, however, numerous instances of instantaneous reactions between non-electrolytes have been observed, this is not an exclusive characteristic of ionised substances.

When dilute solutions of different salts at similar molecular concentrations are mixed without yielding precipitates, there is, as a rule, little or no appreciable heat development. The ionic dissociation hypothesis supplies a simple explanation of this fact. Since most salts are almost completely dissociated even in moderately strong solutions, on these solutions being mixed, the salts will remain ionised; in other words, the only appreciable change which occurs is that each salt now occupies a larger volume than before, in consequence of which small changes in temperature due mainly to 'heat of dilution' may be observed.

The same consideration shows that when, say, sodium chloride and potassium nitrate are dissolved together in water, the ions $Na^{\cdot}$, $K^{\cdot}$, Cl', and NO_3' constitute most of the dissolved matter, though, strictly speaking, there must also be present small quantities of all the four possible salts in a non-ionised condition. Thus there are present in this solution both sodium ions and nitrate ions, and except at infinite dilution these must be in equilibrium with some of the undissociated sodium salt,

$$Na^{\cdot} + NO_3' \longleftrightarrow NaNO_3.$$

Similarly, the following equilibria must also occur:

$$\begin{aligned} Na^{\cdot} + Cl' &\longleftrightarrow NaCl \\ K^{\cdot} + NO_3' &\longleftrightarrow KNO_3 \\ K^{\cdot} + Cl' &\longleftrightarrow KCl. \end{aligned}$$

Evidently, then, except at infinite dilution, which is a purely hypothetical condition, some quantity of all the possible neutral combinations of the oppositely charged ions in a solution must also be present. The amount of any such neutral combination will depend on the number and concentrations of the ions composing it, and also on the peculiarities of the combination itself. If the neutral substance is a weak electrolyte, then it will be formed in large proportion, because at equilibrium it has a relatively small tendency to break down again into its ions. That is, in solutions containing various ions there is a tendency to form those undissociated combinations which are weak electrolytes.

If, for example, solutions of sodium acetate and hydrochloric acid, both strong electrolytes, are mixed, there are present in the first instance the ions $H^{\cdot}$, Cl', $Na^{\cdot}$, and $C_2H_3O_2'$. Of the four possible undissociated combinations—namely, HCl, $NaCl$, $NaC_2H_3O_2$, and $HC_2H_3O_2$—the last is by far the weakest electrolyte. This compound, therefore, is formed at once, and the main change is represented by

$$H^{\cdot} + Cl' + Na^{\cdot} + C_2H_3O_2' = Na^{\cdot} + Cl' + HC_2H_3O_2\,;$$

or, eliminating terms common to both sides,

$$H^{\cdot} + C_2H_3O_2' = HC_2H_3O_2.$$

This explains why the so-called strong acids expel the weak ones from their salts even in moderately dilute solution.

HEAT OF NEUTRALISATION OF ACIDS AND BASES.

Water itself may be regarded as a very weak electrolyte, or possibly even as a non-electrolyte (p 167). It is formed, therefore, when $H^{\cdot}$ and OH' ions are brought together—as, for example, when solutions of an acid and of a basic hydroxide are mixed. The process of neutralisation of potassium hydroxide by hydrochloric acid, both mainly ionised in solution, may thus be expressed by

$$K^{\cdot}+OH'+H^{\cdot}+Cl' = K^{\cdot}+Cl'+H_2O\ ;$$

or, the $K^{\cdot}$ and Cl' ions common to both sides being eliminated, the only appreciable change in the neutralisation process is

$$H^{\cdot}+OH' = H_2O,$$

or the formation of water.

The process does not involve the potassium or chlorine ions, and would be representable in the same way, no matter what the metal in the strong base or the radicle in the strong acid. In accordance with this view, the heat of neutralisation of an equivalent of any strong acid with any strong base should be the same. Experiments show that this is so, the heat of neutralisation being + 13,700 calories for every equivalent neutralised; + 13,700 calories, therefore, is the heat produced when one gram-molecule of water is formed from its ions.

IONIC EQUILIBRIA.

Equilibrium between an undissociated electrolyte and its ions is affected in the same way as equilibrium in ordinary dissociation. Thus, the dissociation of a *binary* electrolyte* being represented by $A \rightleftharpoons B^{\cdot}+C'$, then, if at equilibrium the concentration of $B^{\cdot}$ is increased, the reaction has more opportunity than previously of progressing from right to left, with the result that more A is formed at the expense of C'. In the case of a solution of acetic acid, for example, if the concentration of the $C_2H_3O_2'$ ions is increased, as can be done by adding sodium acetate, then more undissociated acetic acid is formed at the expense of the $H^{\cdot}$ ions, which thus decrease in concentration: the acidity of the solution, therefore, also decreases. Acetic acid (1 of acid in 10 of water) dissolves calcium oxalate or zinc sulphide fairly freely, but in presence of excess of sodium acetate it loses most of its power of dissolving these compounds; even in presence of only one equivalent of sodium acetate it has only one-fortieth of its original strength. The effect of neutral salts is very marked only with the weaker acids; similar effects are noticed with weak bases such as ammonium hydroxide.

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* An electrolyte the molecule of which furnishes two ions only.

Ammonium hydroxide may be represented as dissociated slightly in aqueous solution.

$$NH_4OH \rightleftharpoons NH_4^{\cdot} + OH';$$

but if $NH_4^{\cdot}$ ions, in the form of ammonium chloride, be added to the solution the ionisation of the hydroxide is greatly diminished, and therefore its strength is greatly decreased. For this reason ammonium chloride is added to ammonium hydroxide in order, for example, to prevent the latter from dissolving aluminium hydroxide, which is appreciably soluble in a pure solution of ammonium hydroxide.

If a drop of acetic acid is added to a little water coloured with methyl orange,* the latter is turned red. If now a few crystals of sodium acetate are added, the colour of the indicator becomes yellow, for the acetic acid, though free, is no longer strong enough to act on the methyl orange.

Similarly, if a drop of ammonium hydroxide is added to water which contains a little phenolphthaleïn solution,* the latter is turned pink. If now a little pure solid ammonium chloride is added, the ammonium hydroxide is rendered so weak that the red tint nearly or quite disappears.

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* Methyl orange is the sodium salt of a strong organic acid, the yellow solution of which is turned red by strong acids owing to the formation of undissociated molecules of the organic acid; it is used as an indicator, principally in titrating carbonates of the alkali metals and ammonium hydroxide.

Hence methyl orange is useless as an indicator in titrating relatively weak acids; when the end of the titration is near, the salt which is present reduces the strength of the relatively weak acid to such an extent that the colour gradually fades away before an equivalent quantity of alkali has been added. Similarly, phenolphthalein cannot be used in the titration of ammonium hydroxide, but may be satisfactorily employed in the titration of weak acids with strongly basic hydroxides.

Saturated Solutions of Electrolytes.—When a saturated solution of any solid electrolyte is prepared, there are probably two reversible reactions proceeding simultaneously and at equilibrium; that is to say, when the solution is saturated, the changes going on may be represented by the simultaneous equations:

$$\underset{c_1}{AB}\text{ (solid)} \longleftrightarrow \underset{c_2}{AB}\text{ (dissolved, non-ionised)} \longleftrightarrow \underset{c_3}{A^{\cdot}} + \underset{c_4}{B'}$$

where c_1, c_2, c_3, c_4, represent the active masses (p. 363).

The active mass c_1 is constant, as it is that of a solid; c_2, the active mass of the non-ionised substance, is also constant, for it bears a fixed ratio to c_1 assuming the law of mass-action.

This law would also lead to the following equation for the second reversible reaction:

$$c_3 c_4 = \text{a constant} \times c_2 = \text{a new constant, say } K.$$

That is to say, in the saturated solution of an electrolyte, the product of the concentrations of the ions of the electrolyte would be constant at any given temperature.

This is found to be true in practice, and the product, K, is known as the *solubility product* of the electrolyte.

An electrolyte, therefore, dissolves until the product of the concentration of its ions has reached the value K (of the solubility product), whatever may be the relative concentrations of the ions present in the solution. If the solubility product is exceeded, then the solution is supersaturated; but if the actual product of the ion concentrations is less than the solubility product the solution is unsaturated.

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* Phenolphthaleïn is a colourless lactone of a weak acid; solutions of its ionised salts are pink. It is principally used in titrating weak acids.

If, then, to a saturated solution of any electrolyte another electrolyte giving ions identical with any of those of the first electrolyte is added, then the solubility product is exceeded and the solid separates. Thus, when common salt is added to a soap solution, hard soap may be precipitated, because the concentration of sodium ions is increased, and the solubility product may be exceeded. On the addition of potassium chloride to a solution of a hard or *sodium* soap—say the stearate—soft soap may be precipitated because the product of the concentrations of the $K^{\cdot}$ ions added, and the stearate $'$ ions previously present, may be made to exceed the solubility product of potassium stearate.

The process of precipitating substances by the addition of others containing a common ion is known as 'salting-out.' It is not necessary, however, that both or either of the substances concerned should be salts; thus strong hydrochloric acid precipitates barium chloride and common salt respectively from aqueous solutions of these compounds; similarly, nitric acid precipitates lead nitrate from its solution. Acids may be precipitated by other strong acids or by one of their own salts, and the alkali hydroxides may precipitate calcium and barium hydroxides from their solutions.

The opposite case—namely, an increase in solubility owing to the partial or complete removal of one of the ions of the dissolving substance from the solution—is also frequent and of much importance.

Calcium oxalate is very slightly soluble in water, yielding the ions $Ca^{\cdot\cdot}$ and C_2O_4''; on the addition of a mineral acid, yielding hydrogen ions, some of the C_2O_4'' ions unite with these to form non-ionised $H_2C_2O_4$, or oxalic acid. The calcium oxalate then proceeds to dissolve until its solubility product is again reached. This explains why the salts of weak acids are dissolved freely by mineral acids. Sparingly soluble salts of strong acids are not so much affected, however, because there is not so great a tendency for their negative ions to unite with hydrogen ions, and the equilibrium is not greatly disturbed.

Where an excessively weak acid forms a sufficiently sparingly soluble salt it may be able to expel even a strong acid. Thus, if carbon dioxide is led into lead nitrate solution, carbonic acid and therefore CO_3'' ions are formed, and to such an extent that the product of the concentrations of the $Pb^{\cdot\cdot}$ ions and the CO_3'' ions may exceed the very minute solubility product of lead carbonate; consequently lead carbonate is precipitated, while free nitric acid remains in solution. The solubility product of calcium carbonate, though extremely small, is relatively much greater than that of lead carbonate, and therefore carbon dioxide does not produce a precipitate in a solution of calcium nitrate.

CHAPTER XLIV.

The Halogens.*

The element chlorine (p. 140), which occurs in such large quantities combined with sodium, is closely related in chemical behaviour to three other elements, named respectively *fluorine*, *bromine*, and *iodine*. All these elements are very active, and consequently are not found in nature in the free state; they occur principally in combination with one of the metals sodium, potassium, calcium, and magnesium, and in smaller quantities in combination with silver.

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* The more important generalisations and laws relating to chemical phenomena, and the various hypotheses and theories based on them, have now been discussed. In the following pages many of the more prominent elements and their compounds are described, and the student is introduced

Just as sodium chloride, $NaCl$, and calcium chloride, $CaCl_2$, are salts derived from hydrogen chloride, HCl, so also the naturally occurring compounds of fluorine, bromine, and iodine are salts derived from hydrogen fluoride, HF: hydrogen bromide, HBr; and hydrogen iodide, HI, respectively. From this property of forming substances similar to 'common salt,' the four elements in question are classed together as the *halogens* (salt-producers), and their hydrogen compounds are termed *halogen acids;* the salts derived from these acids are called *haloid salts* or *halides.*

In considering this *family* of elements, the various members will be described in the order of their atomic weights,* a course which will be adopted in the case of other families. This order is,

Fluorine, 19. Chlorine, 35·5. Bromine, 79·9. Iodine, 126·9.

As the important compounds of fluorine are not very numerous, they will be described together with the element in this chapter; further, as hydrogen fluoride is far better known than fluorine, a description of this compound will precede that of the element.

HYDROGEN FLUORIDE, HF.

The more important naturally occurring salts of this acid are *fluor-spar* (*calcium fluoride*) and *cryolite* (p. 402). As the acid is volatile, it is generally prepared by heating powdered calcium fluoride with sulphuric acid,

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

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to a great array of facts which will seriously tax his memory. Little can be done to lighten his task. Elements related in properties are classed together, and cross-references to similar or analogous phenomena are freely given; but unless the foregoing general principles are understood and applied, the facts will remain a mass of disconnected data, and little intelligent progress will be made.

The system on which the elements are classified is described later (p. 713), and need not be considered until most of the more important elements have been studied.

* The atomic weights refer to O=16 (compare p. 460).

Since hydrogen fluoride attacks glass and other materials containing silicates (p. 578), the operation is carried out in a retort made of lead (or of platinum), and the vapour which is evolved is passed into water contained in a leaden vessel. The solution thus obtained is stored in bottles made of gutta-percha, or of glass coated on the inside with a layer of paraffin wax.

The aqueous solution of hydrogen fluoride, known as *hydrofluoric acid*, has the properties of an acid, just as has the aqueous solution of hydrogen chloride. It turns blue litmus red, reacts with hydroxides and oxides, and attacks magnesium, zinc, and iron, forming *fluorides*, with liberation of hydrogen.

The most important practical difference between hydrofluoric acid and the other halogen acids is that the first-named compound acts on silica and on silicates, giving water and (volatile) *silicon tetrafluoride* (p. 578),

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

This property is made use of in etching glass,* and also in detecting hydrogen fluoride and other fluorides in the course of qualitative analysis.

For marking the scales on thermometers, burettes, &c., the clean glass surface is first coated with paraffin wax, which is then scratched off with some sharp instrument to expose those parts which are to be etched. The apparatus is next placed in the vapour of hydrogen fluoride, and after having been etched it is washed well and the wax is removed.

A similar process is used in testing for fluorides. The substance under examination is warmed with sulphuric acid in a leaden basin; the latter is covered with a watch-glass which has been previously coated with paraffin wax, but from certain parts of which the wax has been removed with a knife or a pin. After some time the exposed surface is washed, freed from wax, and examined; if the surface is found to be etched, a fluoride was present.

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* The smooth, lustrous surface of the glass is corroded and becomes dulled because some of its components are removed.

Hydrofluoric acid is also used in the qualitative and quantitative analysis of insoluble silicates. When silica or a silicate is repeatedly evaporated with the acid, the whole of the combined silicon volatilises in the form of silicon tetrafluoride; the silicates are thus converted into fluorides, which may then be transformed into sulphates by heating them with sulphuric acid.

Anhydrous hydrogen fluoride is obtained by heating dry potassium hydrogen fluoride (p. 402) in a platinum retort and collecting the vapour in a cooled platinum receiver. It is a colourless liquid, boiling at 19·5°, and is miscible with water; it has a very pungent odour and is highly poisonous.

It has already been mentioned that at ordinary temperatures the molecules of hydrogen fluoride have the formula $(HF)_2$. This is one of those cases in which it is difficult to say whether the molecules of the formula $H-F$ which exist at higher temperatures have merely associated (p. 384), or whether they have undergone chemical change. It may be that the fluorine atoms become tervalent, and that $(HF)_2$ is a compound of the constitution $H-F=F-H$. The existence of potassium hydrogen fluoride (p. 402) may also be accounted for by supposing that fluorine may be tervalent.

Calcium fluoride, CaF_2, has been known for a long time, and used under the name of *fluor-spar* as a 'flux' in melting ores and salts.

It melts at a bright red heat, and when mixed with other minerals it forms mixtures which may liquefy and flow at a lower temperature than that at which any of the other minerals alone would melt.

It is often found in crystals (cubes or octahedra), which are sometimes colourless, sometimes coloured blue, green, or yellow by the presence of small quantities of other compounds. It is practically insoluble in water, and in this respect differs unexpectedly* from calcium chloride; it is also practically insoluble in acids, but it dissolves chemically in hot concentrated sulphuric acid (see above).

Potassium fluoride, KF, is obtained by neutralising hydrofluoric acid with potassium carbonate, and then evaporating the solution; it crystallises in cubes and is readily soluble in water. When it is dissolved in hydrofluoric acid and the solution is evaporated, crystals of **potassium hydrogen fluoride,** KHF_2 or HF,KF, are deposited. This substance decomposes when it is strongly heated, giving hydrogen fluoride and a residue of potassium fluoride.

Silver fluoride, AgF, may be obtained by dissolving silver oxide in hydrofluoric acid; it is colourless and crystalline, and is readily soluble in water, a property in which it differs in a very unexpected manner* from the silver salts of the other halogen acids (p. 661)

Aluminium fluoride, AlF_3, occurs together with sodium fluoride, NaF, in the mineral *cryolite*, AlF_3, 3NaF, a colourless crystalline complex salt (p. 591) found principally in Greenland. Cryolite is sometimes used as a flux (p. 610).

Small quantities of fluorides occur in the animal kingdom (in the bones, teeth, &c.), in certain plants, and in sea-water.

Fluorine, F_2, At. Wt. 19·0, is so active that although hydrogen fluoride was long believed to be the hydrogen compound of an unknown element, all attempts to obtain this element, by methods such as those which lead to the production of chlorine from hydrogen chloride, were complete failures. The element was at last isolated (Moissan, 1886) by the electrolysis of potassium fluoride dissolved in anhydrous hydrogen fluoride.

The electrolysis was carried out in a platinum U-tube (fig. 97), using platinum electrodes (*a*, *a*) which passed through stoppers of calcium fluoride (*b*, *b*); fluorine was liberated at the positive electrode, and hydrogen (a secondary

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* Unexpected, because most salts of the halogen acids which contain the same metal are very similar in properties (p. 424).

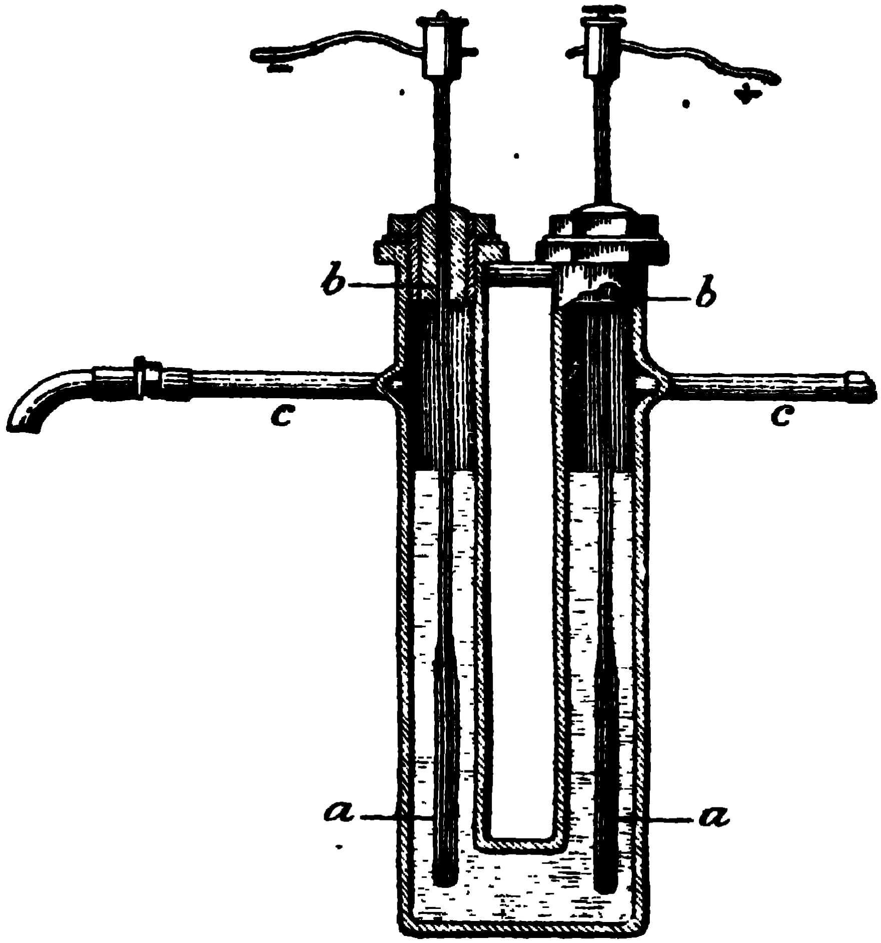

Fig: 97.

product, p. 302, formed by the action of the liberated potassium on the hydrogen fluoride) at the negative electrode.

$$F_2 \leftarrow \begin{matrix} F \vdots K \\ F \vdots K \end{matrix} \rightarrow 2HF = 2KF + H_2.$$

The gases escaped through the side tubes (*c*, *c*), and the fluorine was collected in a platinum observation tube closed with thin plates of transparent fluor-spar. The electrolysis was conducted at a low temperature (– 23°) in order to lessen the action of the fluorine on the platinum.

Fluorine is a gas, having a yellowish-green colour similar to, but paler than, that of chlorine. It decomposes water at ordinary temperatures, forming hydrogen fluoride, and liberating oxygen and *ozone* (p. 461); hence it is absolutely necessary to exclude moisture in the preparation of fluorine. It combines with hydrogen with explosive violence at ordinary temperatures, and most other elements, including carbon, unite with it so vigorously that they take fire in the gas; oxygen and fluorine, so far as is known, do not combine. Fluorine attacks silica (and silicates), silicon tetrafluoride and oxygen being formed.

CHLORINE, Cl_2; AT. WT. 35·5.

Sodium chloride (pp. 35, 147) is by far the most abundant naturally occurring chlorine compound, but potassium chloride or *sylvine*, KCl, is also found in small quantities, either alone or crystallised with magnesium chloride, forming a double salt (p. 322), KCl, $MgCl_2$, $6H_2O$, known as *carnallite;* this double salt occurs principally near Stassfurt in a large saline deposit (p. 676). Silver chloride is found as the mineral *horn-silver*, AgCl; chlorides also occur in all natural waters and in all animals and plants.

When chlorine was first discovered (p. 140), and for some time afterwards, it was supposed to be a compound of oxygen. In those days it was thought that an acid must contain oxygen (p. 248), and therefore it was assumed that hydrochloric acid did so; consequently the gas produced by heating hydrochloric acid with manganese dioxide was regarded as an oxygen compound of hydrogen chloride (Berthollet). Davy showed in 1810 that chlorine is not changed when it is passed over heated carbon, a process which decomposes many oxides; also that although oxygen is evolved when certain metallic oxides (calcium oxide, for example) are heated in chlorine, the quantity of this gas which is liberated is exactly that contained in the given weight of the metallic oxide, so that oxygen is not liberated from the chlorine. These results seemed to show that chlorine was not an oxide, and as there was no evidence that it was a compound, Davy suggested that it should be classed as an element and gave it the name which it now bears. Since those days no fact at variance with this conclusion has been observed.*

Chlorine is liberated when certain chlorides are heated strongly; a few chlorides (auric chloride, platinic chloride) are decomposed into chlorine and metal, others (cupric chloride) into chlorine and a lower metallic chloride, but as a general rule chlorides volatilise at very high temperatures without decomposing.†

The method generally used in preparing chlorine in the laboratory (p. 140) is based on the oxidation of hydrogen chloride with manganese dioxide (p. 286).‡

As native pyrolusite (p. 443) often contains carbonates, it should be first warmed with dilute nitric acid until all carbon dioxide is expelled, and then washed with water, if it is required for the preparation of *pure* chlorine; the gas evolved by heating the pure dioxide with pure hydrochloric acid is washed with water and passed through tubes containing gently heated manganese dioxide in order to free it from hydrogen chloride; it is then dried with the aid of sulphuric acid or phosphorus pentoxide and collected in a suitable glass vessel (fig. 23, p. 68).

Pure chlorine may also be obtained by the electrolysis of fused silver chloride (p. 305), using carbon electrodes.

Since chlorine is formed by the action of hydrogen chloride on manganese dioxide, and hydrogen chloride is generated by the interaction of sulphuric acid and sodium chloride, chlorine may be prepared by gently heating a mixture of sodium chloride (or other metallic chloride), manganese dioxide, and sulphuric acid. The final results of this interaction are expressed by the equation,

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* It is impossible to *prove* that a given substance is an element, because the definition of an element (p. 51) is based on a negative assertion; a substance is considered to be an element unless it can be proved that it is a compound.

† It is possible, therefore, to determine the vapour densities of some chlorides by V. Meyer's method, and thus obtain data from which the molecular formulæ of these chlorides may be deduced.

‡ On the danger of inhaling chlorine, compare p. 140.

$$2NaCl + MnO_2 + 3H_2SO_4 = Cl_2 + MnSO_4 + 2NaHSO_4{}^* + 2H_2O,$$

but these results are doubtless produced by a sequence or combination of the three (or more) simple changes (compare p. 330), namely,

$$(1)\ NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$(2)\ MnO_2 + 4HCl = Cl_2 + 2H_2O + MnCl_2$$
$$(3)\ MnCl_2 + H_2SO_4 = MnSO_4 + 2HCl.$$

Equations such as these, which represent intermediate stages of a reaction, are termed *partial equations*.

The nature of a complex reaction is often rendered more intelligible by the use of partial equations, from which it is then possible to deduce the equation for the complete interaction without having committed this equation to memory. In deducing this expression, those substances which appear in equal quantities on opposite sides in any series of partial equations are merely intermediate products, and are eliminated from the final equation. Thus in the above case one molecule of $MnCl_2$ appears on opposite sides of the equations (2) and (3), so that by combining these in the one expression,

$$(4)\ MnO_2 + 4HCl + H_2SO_4 = Cl_2 + 2H_2O + MnSO_4 + 2HCl,$$

this intermediate product is eliminated.

But in this equation (4), two of the four molecules of HCl on the left appear on the right, so that it may be written,

$$(5)\ MnO_2 + 2HCl + H_2SO_4 = Cl_2 + 2H_2O + MnSO_4.$$

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* The formation of normal sodium sulphate in accordance with the equation,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

only takes place at high temperatures (p. 417).

Next the quantities of the substances represented in the partial equation (1) must be doubled in order to provide the 2HCl necessary for the interaction shown in (5); this leads to

$$(6)\quad 2NaCl + 2H_2SO_4 = 2NaHSO_4 + 2HCl,$$

and finally the partial equations (5) and (6) are combined to give

$$MnO_2 + 2NaCl + 3H_2SO_4 = Cl_2 + 2H_2O + MnSO_4 + 2NaHSO_4.$$

There are many other substances besides manganese dioxide which oxidise hydrogen chloride, liberating chlorine. Lead dioxide, PbO_2 (p. 601), and barium dioxide, BaO_2 (p. 647), are examples. The final results in these cases are similar to those obtained with manganese dioxide,

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$
$$BaO_2 + 4HCl = BaCl_2 + 2H_2O + Cl_2.$$

Red lead, Pb_3O_4 (p. 603), is decomposed by hydrochloric acid, giving lead monoxide, PbO, and lead dioxide, PbO_2; the former dissolves chemically in the acid, giving the *corresponding* salt (p. 284), while the latter gives chlorine, lead chloride, and water, as shown above.

Potassium dichromate (p. 506) also oxidises hydrogen chloride; so also do nitric acid (footnote, p. 236) and bleaching powder (pp. 286, 639). Chlorine is very conveniently prepared by dropping hydrochloric or dilute sulphuric acid from a tap-funnel on to bleaching powder.

Chlorine is prepared *commercially* in several ways: (1) By heating manganese dioxide with commercial hydrochloric acid (p. 274); in this case the manganese dioxide is regenerated by the Weldon process (p. 447). (2) By passing a mixture of air and hydrogen chloride through chambers in which porous earthenware (baked clay), previously soaked in a solution of copper sulphate, is heated at about 380°. (3) By the electrolysis of a solution of sodium chloride (pp. 303, 672).

The reactions which occur in process (2) are not known, but the final result is the oxidation of the hydrogen chloride by atmospheric oxygen; the copper sulphate, or traces of cupric chloride, $CuCl_2$, formed from it, acts as a catalytic agent (pp. 233, 288).

Chlorine unites directly with nearly all other elements, but not with oxygen, nitrogen, or carbon;* chlorine compounds of these elements may be obtained by indirect processes, but compounds of chlorine with fluorine and the members of the argon family (p. 681) are unknown.

Chlorine also combines directly with some chlorides ($CuCl$, $FeCl_2$, and PCl_3, for example), the higher chlorides ($CuCl_2$, $FeCl_3$, PCl_5) being formed.

Most metallic oxides are decomposed by chlorine at high temperatures with liberation of oxygen,

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$

Chlorine generally attacks compounds which contain hydrogen, as, for example, water (p. 285), hydrogen sulphide (p. 285), and ammonia (p. 521); in such cases hydrogen chloride is formed, and the element which was combined with the hydrogen is either liberated in the free state (p. 145) or unites with chlorine, according to the conditions and the nature of the element.

Chlorine is easily condensed to a liquid, and the liquid, contained in steel cylinders, is an article of commerce.

When ice-cold water is saturated with chlorine a yellow crystalline substance, often called *chlorine hydrate*, separates. The composition of this substance is $Cl_2, 10H_2O$; it decomposes at ordinary temperatures.

BROMINE, Br_2; AT. WT. 79·9.

The principal compounds of bromine which occur in nature correspond with those of chlorine, but are far less abundant;

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* The expression 'unites directly' means that the two elements, *as such*, combine together; chlorine does not act on carbon, but it reacts with carbon disulphide (footnote, p. 216), giving carbon tetrachloride, CCl_4.

sea-water, for example, contains only about 3 parts of combined bromine to every 1000 parts of combined chlorine, and relatively very small quantities of bromides are found in natural waters.

Bromine was first obtained by Balard in 1826 from the mother-liquor which remains when sea-water is concentrated to such an extent that most of the sodium chloride is deposited.

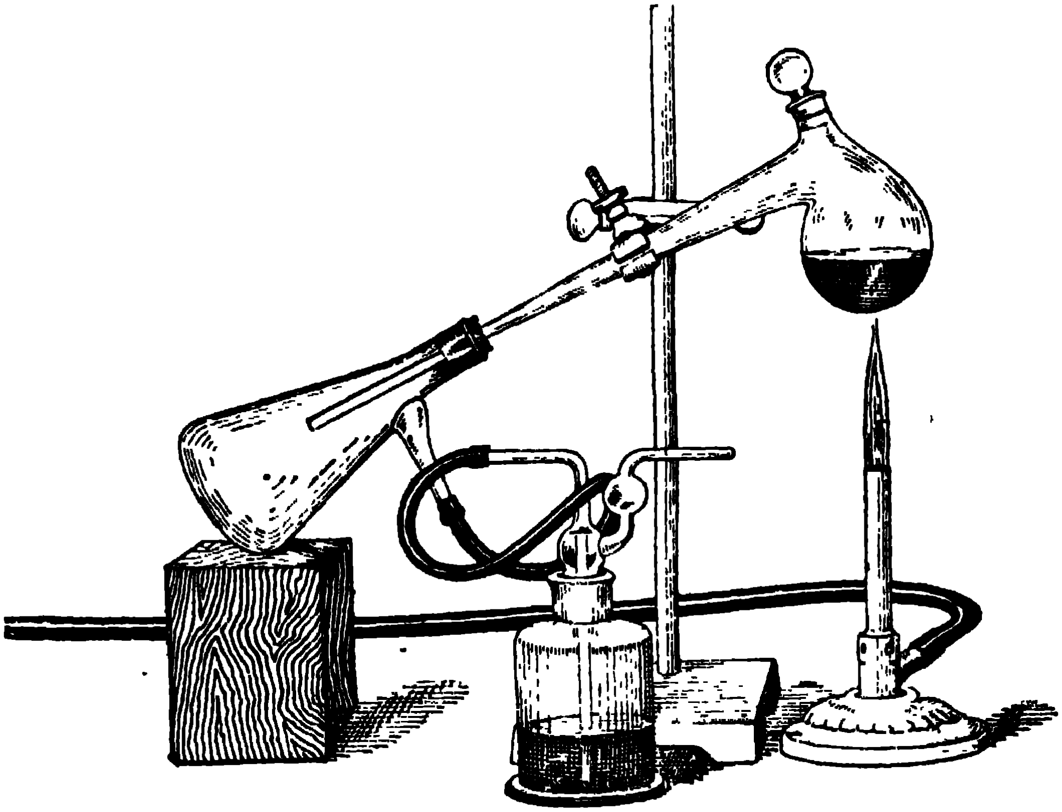

Fig. 98.

It is easily liberated by oxidising hydrogen bromide, HBr, with manganese dioxide, or with any of the other oxidising agents mentioned in describing chlorine (p. 407). In the laboratory bromine is usually prepared by gently heating a mixture of sodium bromide and manganese dioxide with sulphuric acid in a retort (fig. 98),

$$2NaBr + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2.^*$$

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* Compare preparation of chlorine, p. 406.

The reddish-brown vapour which is evolved is passed into a receiver cooled in ice,* and the receiver is connected with a wash-bottle containing water, so that no vapour escapes into the room.†

The liquid thus obtained is freed from hydrogen bromide by distilling it with a little manganese dioxide, and from water by shaking it with concentrated sulphuric acid, in which it is insoluble. If pure materials have been used the element is then pure.

On the large scale bromine is manufactured from the bromides occurring in certain natural waters, in sea-water, or in the mother-liquors obtained in crystallising the salts of the Stassfurt deposits (p. 676). These solutions, which contain other halogen salts, are concentrated, and the chlorides and sulphates which crystallise out are removed; the mother-liquors are then heated with manganese dioxide and sulphuric acid, or treated with chlorine, or submitted to electrolysis (p. 672). The liberated bromine is then volatilised and the vapour is condensed.

Commercial bromine may contain many impurities such as hydrogen bromide, chlorine, iodine, and bromoform, and the pure element is best prepared from purified sodium bromide as described above.

Sodium bromide, which is itself prepared from commercial bromine, is purified by recrystallisation from water, and is freed from iodide by treating it with a little bromine; the bromine prepared from this sodium bromide is distilled with sodium bromide to free it from chlorine, and is then used to prepare pure sodium bromide (p. 433).

Bromine melts at −7·5°, and at ordinary temperatures is a dark reddish-brown liquid, the vapour of which has an intensely disagreeable and irritating smell. The vapour should not be deeply inhaled even in small quantities, as it seriously affects the respiratory organs, but the smell of the diluted vapour may be cautiously examined. The liquid has a sp. gr. 2·99 at 15°, and boils at about 63°. Bromine is soluble in about 33 times its own volume of water, giving a yellowish-brown solution (*bromine water*), but it is much more soluble in an aqueous solution of sodium bromide, and is miscible with many liquid carbon compounds such as carbon disulphide and chloroform.

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* The vessel containing the ice is omitted from the figure for the sake of clearness.

† Bromine is very poisonous and extremely corrosive.

In chemical properties bromine is very similar to chlorine, and is a very active element. Although it does not unite with oxygen, it combines directly with most of the common elements, whether non-metals or metals, in some cases with great violence. When, for example, a small piece (say 0·5 gram) of phosphorus is dropped into a test-tube containing bromine (say 2 c.c.) an *explosive* reaction occurs, and a yellow crystalline compound, *phosphorus pentabromide*, PBr_5, is formed.* When powdered antimony is dropped into excess of bromine, *antimony tribromide* is formed with development of light and heat, a violent reaction taking place.*

Bromine, like chlorine, acts on many compounds of hydrogen, and combines with the hydrogen, forming hydrogen bromide (p. 418); it is therefore an oxidising agent. Bromine water is also a very useful oxidising agent; although bromine does not decompose water appreciably except in direct sunlight, the reversible reaction,

$$H_2O + Br_2 \longleftrightarrow HBr + HBrO,$$

takes place rapidly from left to right in presence of some substance which decomposes the hypobromous acid, HBrO, and thus diminishes its concentration (p. 355). Hence in presence of water, bromine, like chlorine, oxidises certain coloured compounds to colourless ones; that is to say, it bleaches them.

Free bromine, even if present in very small quantities only, may be detected by its colour and by its smell (cautiously observed); in very minute quantities, by extracting it from the solution or gas in which it is contained with carbon disulphide, and then shaking the extract with potassium iodide and starch solution, when a blue colouration due to the liberation of iodine is produced (p. 415). Chlorine and many other substances also give this reaction.

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* In all experiments with bromine great care should be taken to protect the eyes as well as the lungs.

Bromine is not much used except in the laboratory, but bromides are employed in photography and in medicine; these bromides are all originally prepared from bromine.

IODINE, I_2; AT. WT. 126·9.

Although iodides are very widely diffused and occur in many natural waters, as well as in sea-water, they are present in quantities so extremely small that their presence is difficult to detect. Fortunately many animals and plants (sponges, seaweeds) which live in sea-water have the property of abstracting combined iodine (and combined bromine) from the water and concentrating it in their tissues;* consequently seaweed is an important, and until recently was the only, source of the iodine and iodides of commerce, which are now also obtained from Chili saltpetre (caliche, p. 414).

Iodine was discovered by Courtois in 1812 in a sample of sodium carbonate which had been prepared from the ashes of plants, these plants having grown near the sea-shore. It is generally prepared in the laboratory by heating a mixture of sodium iodide and manganese dioxide with sulphuric acid in a retort; the violet vapour which is evolved condenses to steel-blue crystals in the neck of the retort and in the receiver,

$$2NaI + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + I_2.\dagger$$

The apparatus which is employed is the same as in the preparation of bromine (fig. 98, p. 409), but the receiver need not be cooled with ice. With pure sodium iodide and other pure materials, the iodine obtained is free from any appreciable quantity of impurity.

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* Iodides also occur in minute quantities in some fresh-water plants and in terrestrial animals. The thyroid gland of man and of many animals contains notable quantities of combined iodine, and this element seems to be essential to the life of the higher organisms.

† Compare preparation of chlorine, p. 406.

In the preparation of iodine commercially, sun-dried seaweed is burnt in shallow pits (or is submitted to destructive distillation, p. 114), and the ash known as *kelp* or *varec* is extracted with water.

From the aqueous extract a large proportion of the chlorides, sulphates, and carbonates of sodium and potassium is separated by crystallisation, and the mother-liquor is then treated with sulphuric acid in order to decompose sulphides and thiosulphates (p. 496).* The sodium sulphate which is formed in this decomposition may also be removed by crystallisation.

The liquors (which contain chlorides, bromides, and iodides) are placed in iron retorts, sulphuric acid is added, and then a relatively *small quantity* of manganese dioxide; on their being heated, iodine is liberated and the vapour is condensed in a series of earthenware vessels. A little more manganese dioxide is then added, and the heating is continued; these operations are repeated until the addition of manganese dioxide causes the liberation of bromine, at which point distillation is stopped. The liquors remaining in the still are afterwards used for the preparation of bromine.†

Instead of distilling kelp or varec liquors with manganese dioxide and sulphuric acid, they may be treated with chlorine in quantities just sufficient to liberate the iodine,

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* Sulphides are formed from the sulphates by reduction during the burning of the seaweed. Thiosulphates are produced by the atmospheric oxidation of the sulphides in aqueous solution (p. 496).

† On manganese dioxide being added in small quantities at a time to a solution of chlorides, bromides, and iodides in presence of sulphuric acid, all three halogens may be momentarily and locally liberated by the oxidation of the halogen acids contained in the liquid; but so long as hydriodic acid is present in sufficient quantity neither bromine nor chlorine escapes from the solution, because both these elements immediately act on the hydrogen iodide, liberating iodine. When, however, the hydrogen iodide has all been oxidised by the manganese dioxide, bromine begins to escape; chlorine is not evolved until all the hydrogen bromide has been oxidised, because it acts on the latter, liberating bromine.

$$2NaI + Cl_2 = 2NaCl + I_2,$$

which is precipitated as a solid and is separated by filtration.*

A much more important source of iodine is a saline mineral called caliche, which occurs in Peru, and which is essentially the same as Chili saltpetre (p. 241). Caliche consists principally of sodium nitrate, but also contains chlorides and iodates (probably potassium iodate, p. 436). When it is purified by recrystallisation from water, the iodates remain in the mother-liquor,† and from the latter iodine is precipitated by adding sulphurous acid or sodium hydrogen sulphite,

$$2KIO_3 + 5H_2SO_3 = K_2SO_4 + 4H_2SO_4 + H_2O + I_2.$$

Commercial iodine may contain bromine, chloride of iodine (p. 429), salts, and moisture. It is purified by dissolving it in an aqueous solution of potassium iodide (see below), and then precipitating it from the filtered solution by adding water;‡ it is afterwards dried on porous earthenware over sulphuric acid, and is finally sublimed (p. 19).

Iodine is a lustrous, grayish-black crystalline substance, which in thin layers is transparent, showing a brownish-red colour. Its sp. gr. is 4·95 at 17°. It melts at 115° and boils at 184°, but it vaporises even at ordinary temperatures, and sublimes readily at temperatures below its melting-point; its vapour has a beautiful purple colour and a characteristic smell.

Iodine is only very sparingly soluble in water, but it dissolves much more freely in an aqueous solution of potassium iodide, and also in many liquid carbon compounds;

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* Although chlorine also liberates bromine from bromides, bromine is not set free in this process until all the iodides have been decomposed, because bromine liberates iodine from iodides.

† Not because the iodates are more readily soluble than the other salts, but because they are present in so small a quantity that the solution is not saturated with them (p. 32).

‡ Iodine acts on filter-paper of poor quality, for which reason filters of glass-wool or asbestos are employed.

its solution in alcohol, ether, or acetic acid is brown, like the solution in water, but its solutions in chloroform and carbon disulphide have a purple colour, like that of iodine vapour.*

Iodine is very similar to bromine in chemical properties, but is not so active; it does not unite directly with oxygen, but it does so with some non-metals and with many metals. When (colourless) phosphorus is placed on iodine it takes fire spontaneously, and if free access of air is prevented (to avoid the formation of phosphorus pentoxide) most of the phosphorus is converted into a yellow solid, *phosphorus triiodide*, PI_3. When mercury and iodine are rubbed together a green powder (which probably contains mercurous iodide), or a scarlet substance (mercuric iodide, HgI_2), or a mixture of the two, is produced, according to the relative quantities of the two elements.

Iodine, like bromine and chlorine, is an oxidising agent, but its oxidising action is almost entirely confined to reactions which occur in presence of water. Thus it oxidises hydrogen sulphide in aqueous solution (p. 339), and also sulphurous acid,

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

The latter reaction is a readily reversible one, and at ordinary temperatures hydrogen iodide is oxidised by concentrated sulphuric acid, but in presence of excess of water the reaction proceeds from left to right until it is practically complete.

Free iodine gives a beautiful and very delicate colour-reaction with an aqueous solution of starch or with starch-paste (p. 125), the addition of a minute quantity of the *free* element producing a dark-blue colour, which disappears on warming the solution or paste, but comes again on cooling. *Combined* iodine, that is to say, an iodide or other iodine compound, does *not* give this colouration.

Since iodine is liberated from iodides by chlorine, bromine, ozone (p. 462), nitric acid, nitrous acid, and nitrogen tetroxide, by hydrogen peroxide in presence of an acid (p. 473), and by many other oxidising agents, and the liberated iodine may be easily detected with the aid of starch, these facts are utilised in testing for the various substances just named. Strips of paper coated with a little starch-paste containing potassium iodide (starch-potassium-iodide papers) are used for this purpose; the papers are moistened and exposed to the gas, or immersed in the liquid, which is to be tested for the oxidising agent. Obviously since so many substances liberate iodine, the appearance of the blue colour is not a distinctive test in any way, and the presence of any suspected substance must be confirmed by other methods.

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* It is not exactly known why some solvents give brown, others violet, solutions, but it is believed that in the brown solutions some of the iodine combines with the solvent.

An important method for the estimation of iodine is described later (p. 497).

Iodine is used in medicine and in the manufacture of all iodides and iodine compounds (such as iodoform), many of which are used as drugs or antiseptics, and in photography.

CHAPTER XLV.

The Halogen Acids.*

Hydrogen chloride, HCl (p. 142), is formed when a mixture of hydrogen and chlorine is ignited, or exposed to direct sunlight, or to the light given out by burning magnesium, a violent explosion taking place unless one of the gases is present in very great excess.

A mixture of hydrogen and chlorine in approximately equal volumes may be conveniently prepared by the electrolysis of concentrated hydrochloric acid in the apparatus shown in fig. 44, but using carbon instead of platinum electrodes. This experiment must be conducted in a dimly lighted room, and the explosive mixture must be very cautiously used.

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* It must be remembered that hydrogen fluoride (p. 399) is one of the halogen acids.

In preparing hydrogen chloride use is made of the fact that sulphuric acid decomposes sodium chloride and other chlorides (p. 359). When the reaction occurs at ordinary temperatures sodium hydrogen sulphate (p. 258) is formed, and when pure materials are used *pure* hydrogen chloride is evolved,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

At much higher temperatures two molecules of sodium chloride may be decomposed by one molecule of the acid, because the sodium hydrogen sulphate which is first produced also acts on sodium chloride,

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

Commercial hydrochloric acid, which is obtained as a by-product in the Leblanc process (p. 274), very often contains arsenic and iron as chlorides, chlorine, sulphur dioxide, sulphuric acid, and dissolved salts such as sodium chloride. The source of many of these impurities is the commercial oil of vitriol, made from iron pyrites (p. 221) by the 'leaden chamber process' (p. 287), and the purification of commercial hydrochloric acid is a troublesome operation seldom attempted.

The nature of the impurities in a commercial product may often be foretold by considering what impurities (1) may be present in the materials used, or (2) may be derived from the materials of the apparatus, or (3) may be present as the result of secondary reactions. Now 'chamber acid,' made from pyrites, often contains arsenic compounds which, in the preparation of hydrogen chloride, give (volatile) arsenic trichloride; also oxides of nitrogen, which are acted on by the hydrogen chloride, giving chlorine. Sulphur dioxide may be formed by the decomposition of sulphuric acid at high temperatures, and some sulphuric acid may volatilise together with the hydrogen chloride; chloride of iron and dissolved salts may be derived from the apparatus.

When concentrated hydrochloric acid (p. 143) is heated, hydrogen chloride is evolved and the solution begins to boil at about 60°, but the boiling-point rises continuously until it reaches and becomes *constant* at 110° under a pressure of 760 mm. The liquid which distils at this constant temperature is constant in composition, and contains 20·2 per cent. of hydrogen chloride; but when the pressure is altered, a liquid having a different boiling point and a different composition ultimately distils over. When very dilute hydrochloric acid is heated the liquid begins to boil just above 100°, and water passes over; the boiling point then begins to rise, and finally reaches 110° (under a pressure of 760 mm.), at which temperature the same liquid of constant boiling-point is obtained as when the process starts with the concentrated acid.

The very great solubility of hydrogen chloride in cold water, compared with the solubility of gases such as oxygen, hydrogen, and nitrogen, seems to show that hydrogen chloride, like sulphur dioxide (p. 233), carbon dioxide (p. 271), and ammonia (p. 266), combines with water to form some soluble compound, which, however, is unstable, and decomposes when the solution is heated. This view accords with the fact that the behaviour of hydrogen chloride towards water is not expressed by Henry's law (p. 164).

The weight of hydrogen chloride contained in a given weight or volume of hydrochloric acid may be determined by titration (p. 256) if no other acid is present, or by precipitation with silver nitrate (p. 149) if other chlorides, &c., are absent. As the specific gravities of solutions of hydrogen chloride of all possible concentrations have been recorded, the percentage of dissolved gas may also be determined by finding the specific gravity of the solution, provided that no other substance is present.

HYDROGEN BROMIDE, HBr.

Bromine and hydrogen unite only when they are heated together. A flame of burning hydrogen continues to burn in bromine vapour, and hydrogen bromide is also formed when a mixture of hydrogen and bromine vapour is passed through a glass tube containing pumice-stone which is maintained at a dull red heat. The reaction is readily reversible.

Hydrogen bromide is *not* prepared by heating a bromide with sulphuric acid, because it is less stable (p. 333) than hydrogen chloride and is decomposed by hot concentrated sulphuric acid, in accordance with the following equation,

$$2HBr + H_2SO_4 \longleftrightarrow Br_2 + SO_2 + 2H_2O.$$

It may be obtained by very carefully adding water to phosphorus tribromide (p. 544) or phosphorus pentabromide (p. 545), which is contained in a flask provided with a tap-funnel and a delivery-tube,

$$PBr_3 + 3H_2O = 3HBr + P(OH)_3$$
$$PBr_5 + 4H_2O = 5HBr + H_3PO_4.^*$$

It is, however, much more conveniently prepared by decomposing phosphorus pentabromide with the water of hydration contained in some suitable salt; under these conditions the reaction is more easily regulated, and the theoretical quantity of water may be used. For this purpose 5–10 grams of borax (hydrated sodium tetraborate, p. 607) are placed in a flask, and 10–20 grams † of coarsely crystalline phosphorus pentabromide are added. The flask is immediately closed with a cork, through which passes a delivery-tube leading to the bottom of a dry gas-jar. On the contents of the flask being shaken cautiously, hydrogen bromide is rapidly evolved; ‡ when the reaction slackens, the contents

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* This equation probably summarises the two changes expressed by the partial equations,

$$PBr_5 + 5H_2O = 5HBr + P(OH)_5 \text{ and } P(OH)_5 = PO(OH)_3 + H_2O.$$

† Compare footnote ‖, p. 62, on quantities. The quantities of these substances required to produce a certain volume of the gas may, of course, be calculated.

‡ For convenience in shaking, a very short delivery-tube is passed through the cork, and this is connected with a longer glass tube by means of india-rubber tubing.

of the flask are gently warmed. The gas is collected by the upward displacement of air (p. 66) or over mercury, and is sufficiently pure for ordinary purposes.

Hydrogen bromide is often prepared by *very cautiously* adding bromine, drop by drop, to *red* phosphorus (fig. 99) in presence of water. The reaction is at first a very violent one, flashes of light are seen, and an explosion may occur unless care is taken. It may be supposed that the phosphorus and bromine combine to form phosphorus tribromide, which is then decomposed (see above), the final results being expressed by the equation,

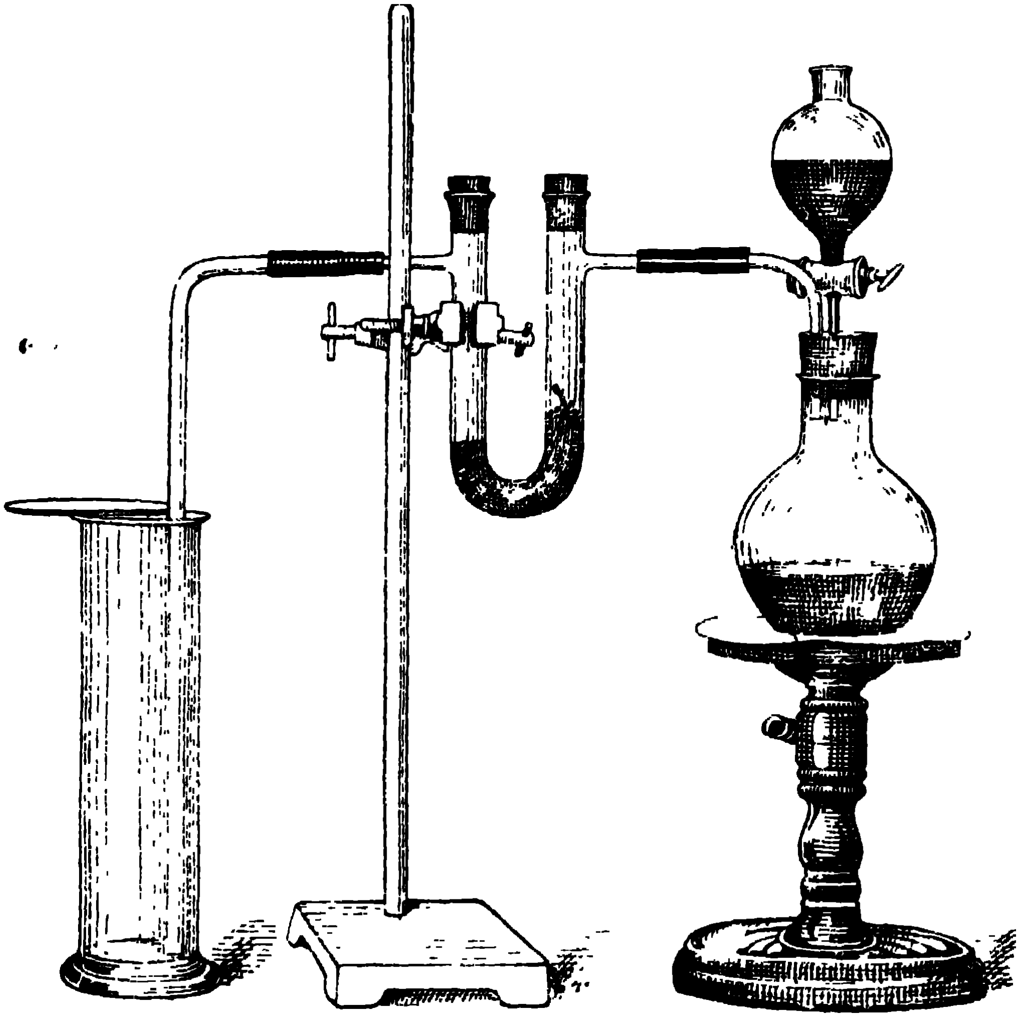

Fig. 99.

$$P_4 + 6Br_2 + 12H_2O = 12HBr + 4H_3PO_3.$$

The escaping hydrogen bromide contains bromine vapour, and is led through the **U**-tube, which contains a very *loosely* packed mixture of broken glass and damp red phosphorus; the bromine is thus converted into hydrogen bromide. The gas may be dried by passing it through vessels containing phosphorus pentoxide (not sulphuric acid).

An aqueous solution of the gas may be prepared by passing hydrogen sulphide through bromine water, under which is a layer of bromine,

$$SH_2 + Br_2 = 2HBr + S\ ;\text{*}$$

the precipitated sulphur is afterwards separated by filtration, and the hydrobromic acid is purified by distillation.

Hydrogen bromide is a colourless gas which fumes in moist air; it is very similar to hydrogen chloride in most respects, but is not so stable (p. 419).

The aqueous solution, *hydrobromic acid,* behaves very like hydrochloric acid: when a cold saturated solution is heated it loses hydrogen bromide and becomes more and more dilute, until at 126 (760 mm. pressure) a liquid of constant boiling-point which contains 47·4 per cent. of hydrogen bromide passes over. The same liquid is ultimately obtained when a more dilute solution is distilled.

HYDROGEN IODIDE, HI.

Hydrogen and iodine do not combine to any appreciable extent except at high temperatures, and as hydrogen iodide is decomposed by sulphuric acid even more readily than is hydrogen bromide (p. 419), it cannot be prepared by heating an iodide with sulphuric acid.

In preparing hydrogen iodide in the laboratory water may be slowly dropped on phosphorus triiodide,

$$PI_3 + 3H_2O = 3HI + P(OH)_3,$$

or water may be slowly added to a mixture of iodine and *red* phosphorus. In the latter case it may be supposed that the first stage in the reaction is the combination of the two elements to form phosphorus triiodide, which then undergoes hydrolysis as shown above.

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* Although the molecular formula of sulphur is S_8 (and strictly speaking the expression S is incorrect), the use of the molecular formula leads to such complex equations that it is seldom employed.

As in the case of hydrogen bromide (p. 419), the water required for the interaction is most conveniently derived from some hydrated salt such as borax, and hydrogen iodide is therefore prepared as follows.

Dry red phosphorus * and dry iodine are ground together in a mortar, and the mixture is placed in a flask containing borax. The delivery-tube of the flask may be connected with a bulb-tube which contains very loosely packed broken glass, or glass beads, mixed with some (not too damp) red phosphorus. On the contents of the flask being cautiously shaken, hydrogen iodide is evolved,† and later on the contents of the flask are gently heated; any iodine which is volatilised is converted into hydrogen iodide by the damp red phosphorus in the bulb. If a considerable *excess* of phosphorus is mixed with the iodine in the flask this bulb is hardly required. The gas may be collected by the upward displacement of air or over mercury.

The apparatus used in preparing hydrogen iodide by dropping water on to a mixture of iodine and red phosphorus is similar to that shown in fig 99. The gas may be dried with the aid of phosphorus pentoxide.

An aqueous solution of hydrogen iodide is conveniently prepared by passing hydrogen sulphide into water which contains dissolved and undissolved iodine,

$$SH_2 + I_2 - 2HI + S;$$

the solution is ultimately filtered from the precipitated sulphur, and is then distilled.

Hydrogen iodide is a colourless gas which fumes in moist air; it closely resembles hydrogen bromide, but is less stable than the latter. Its aqueous solution, *hydriodic acid*, resembles hydrobromic acid; the liquid of constant boiling-point (namely, 127° under 774 mm. pressure) which is finally obtained when concentrated or dilute solutions of hydriodic acid are distilled contains 57 per cent. of hydrogen iodide.

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* The quantities of red phosphorus, iodine, and borax required to yield a certain volume of the gas may be calculated; the phosphorus is used in excess.

† Compare footnote ‡, p. 419, as regards rubber connection. Phosphonium iodide (p. 541) is formed in this experiment, and care should be taken that no part of the apparatus gets blocked by this solid.

Hydriodic acid soon becomes brown when kept, especially in bright sunlight, owing to the oxidation of the hydrogen iodide by atmospheric oxygen. In order to reconvert the iodine into hydrogen iodide, such brown solutions may be treated with a sufficient quantity of red phosphorus (see above), and then distilled to free them from phosphorous acid.

All those substances which liberate iodine from potassium iodide (p. 415) oxidise hydrogen iodide to iodine, and the formation of hydrogen iodide is probably the first stage in the reaction when the oxidising substance is an acid.

Hydrogen iodide dissociates when it is heated above 180°, giving iodine and hydrogen,

$$2HI \longleftrightarrow H_2 + I_2.$$

At 445° equilibrium is attained when 21·5 per cent. of the compound is decomposed; the addition of hydrogen, or of iodine vapour, to the compound diminishes the amount of dissociation in accordance with the principles already explained (p. 366).

Hydriodic acid is used as a reducing agent, chiefly in working with organic compounds, which are heated with the concentrated acid in sealed tubes at a temperature of about 250°. The hydrogen iodide dissociates, and thus provides the hydrogen necessary for the reduction.

THE RELATIONSHIP BETWEEN THE HALOGENS.

Although the four halogens are very different from one another in physical properties at ordinary temperatures, they are very closely related in their general chemical behaviour;

that is to say, if one of them is known to combine with a given element, it may be presumed that the other three will do so likewise, and that the four compounds thus formed will be closely related in properties.

Now, on considering the molecular formulæ of the compounds which the halogens form with any given element, it is evident that these compounds are all of the same *type;* the molecules of these compounds contain the same number of atoms of a halogen united with a fixed number of atoms of the other element. Thus the hydrogen compounds of the halogens are HF, HCl, HBr, and HI; the sodium compounds are NaF, NaCl, NaBr, and NaI; the calcium compounds are CaF_2, $CaCl_2$, $CaBr_2$, and CaI_2; and so on.

This similarity in type of corresponding halogen compounds is due to the fact that in all such corresponding compounds the four halogens have the same *valency* (p. 206). As the physical and chemical properties of compounds depend very greatly on the structure (p. 331) of their molecules, and as the structure of a molecule is closely connected with the valencies of the elements contained in it, elements of similar valency form compounds of similar structure, and these compounds are similar in physical and chemical properties.

The relationship between the four halogens is most clearly brought out by arranging them in the order of their *atomic weights.* When this is done certain marked regularities are observed. In the first place, all the *physical* properties of the four elements and those of any series of corresponding halogen compounds show a *gradual* change in passing from fluorine to iodine, or from the fluorine to the iodine compound.

This regularity is illustrated by the following data:

	Molecular Formula.	Atomic Weight.	M.P.	B.P.	Sp. Gr. of Liquid or Solid.
Fluorine .	F_2	19	-210°	-186°	1·14.
Chlorine .	Cl_2	35·5	-102°	- 35°	1·33 at b.p.
Bromine .	Br_2	79·9	- 7·5°	+ 63°	3·18 at 0°
Iodine .	I_2	126·9	+115°	+180°	4·95 at 17°

	Molecular Formula.	M.P.	B.P.	Density of Gas.
Hydrogen fluoride	HF	--	+19°*	10
Hydrogen chloride	HCl	-111°	-84°	18·2
Hydrogen bromide	HBr	- 88°	-65°	40·5
Hydrogen iodide	HI	- 51°	-34°	64

	Molecular Formula.	Sp. Gr.	Solubility in water at 0°.
Sodium fluoride . .	NaF	2·8 †	4·8 (at 16°)
Sodium chloride . .	NaCl	2·1	35·7
Sodium bromide . .	NaBr	3·0	77·5
Sodium iodide . .	NaI	3·5	158·0

In the second place, the chemical properties of the four elements and those of any four corresponding halogen compounds are very similar, but at the same time there is a gradual change in passing from fluorine to iodine or from a fluorine to an iodine compound. Take as an example the behaviour of the halogens towards hydrogen. They all combine with this element to form a compound of the type HX, which is a monobasic acid, all these acids are very similar to one another in general chemical behaviour, but at the same time the temperature at which the halogen combines with hydrogen gradually rises, and the chemical properties of the acids thus formed show a gradual change. Hydrogen and fluorine combine rapidly even in the dark; hydrogen and chlorine do not combine appreciably in the dark, but do so rapidly in sunlight at ordinary temperatures; hydrogen and bromine do not combine appreciably unless they are gently heated together; hydrogen and iodine do not combine unless they are heated together at a dull-red heat. No matter what property of the acids is considered, there is almost invariably this gradual variation in passing from hydrogen fluoride to hydrogen iodide.

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[*] The high boiling-point of hydrogen fluoride in comparison with those of the other halogen acids is doubtless due to the association (p. 384) of the molecules of the acid.

[†] The first member of a family often shows a somewhat 'abnormal' behaviour.

The difference in behaviour and the gradual variation in properties of the halogen acids are most definitely expressed in terms of the heats of formation (p. 337) of the four compounds from the gaseous elements; the values are as follows,

$$H_2 + F_2 = 2HF + 37,600 \times 2 \text{ calories.}$$
$$H_2 + Cl_2 = 2HCl + 22,000 \times 2 \quad \text{"}$$
$$H_2 + Br_2 = 2HBr + 8,400 \times 2 \quad \text{"}$$
$$H_2 + I_2 = 2HI - 6,000 \times 2 \quad \text{"}$$

It is thus seen that whereas the first three compounds are exothermic, but with decreasing heats of formation, hydrogen iodide is endothermic; this explains to some extent why the reactions expressed by these equations take place with diminishing readiness (p. 338); also why bromine readily displaces iodine from hydrogen iodide and chlorine displaces bromine from hydrogen bromide. Conversely, it would seem that the displacement of bromine by iodine, or of chlorine by bromine, does not occur to any appreciable extent, because the reactions would be strongly endothermic.

Similar gradations and relationships to those observed in the case of the halogen acids are met with on comparing the physical and chemical properties of any other set of corresponding halogen compounds; the four halogens, therefore, form a **natural family.**

Since the halogens form a natural family, their study is facilitated to some extent, because many facts which before seemed to be isolated now become correlated and are easier to remember. Having learnt, for example, that calcium chloride has the formula $CaCl_2$, one might infer by analogy that calcium iodide would exist and have the formula CaI_2; and knowing that calcium chloride is colourless, crystalline, and soluble in water, one might also infer that calcium iodide would show similar properties.

In the case of the halogen family most of the inferences based on analogy would be correct, because the relationship is particularly close and the regularities are very well marked.

But even in this family (and much more so in others which will be described later) the elements or their compounds may show a wholly unexpected or abnormal behaviour in respect to some particular property or properties. Thus the boiling-point of hydrogen fluoride is *higher* than that of hydrogen chloride. Calcium fluoride is insoluble in water, whereas the other three calcium halides are readily soluble. Silver fluoride is soluble in water, whereas the other three silver halides are insoluble. Facts such as these and other cases of abnormal behaviour should be carefully noted, otherwise incorrect inferences may be based on the knowledge that on the whole the halogens are very closely related.

The members of a natural family are generally found together in nature and in a similar state of combination owing to the similarity in properties of their corresponding compounds. For the same reason the elements of a natural family or their corresponding compounds are often separated from one another only with difficulty. Sodium chloride, for example, cannot be completely separated from sodium bromide by fractional crystallisation (p. 32), and it is very difficult to separate silver chloride from silver bromide by any direct process.

The members of a natural family are generally prepared by similar methods, as are also their corresponding compounds, unless the particular method becomes inapplicable owing to the gradual change in properties which invariably occurs. For example, all the halogens may be prepared by the electrolysis of their sodium compounds, but in the case of fluorine the process must be carried out in absence of water. Chlorine, bromine, and iodine may be easily obtained by the oxidation of their hydrogen compounds, but this method is not applicable in the case of fluorine unless every trace of water is excluded. All the halogen acids are liberated from their salts by sulphuric acid, but as sulphuric acid oxidises hydrogen iodide and hydrogen bromide, only the chlorine and fluorine compounds are prepared in this way.

The halogen compounds of the non-metals are as a rule *completely* hydrolysed by water, giving a halogen acid and the hydroxide (acid) of the non-metal, and the reaction is not appreciably reversible (p. 361); the most notable exception is carbon tetrachloride, which is not decomposed even by boiling water. The halogen compounds of the metals, as a rule, are soluble in and are not decomposed by water, or, if they are hydrolysed, the reaction is reversed in presence of excess of hydrochloric acid (p. 362). The common insoluble metallic halides are the silver, mercur*ous*, and cupr*ous* compounds; the lead salts are only sparingly soluble.

The separation of chlorine, bromine, and iodine from one another when they are present in mixtures of their compounds may be accomplished in various ways;* but as the elements are so similar in chemical properties it is not easy to obtain a complete separation.

In one method the solution containing the salts of the three halogen acids is treated with dilute sulphuric acid and potassium nitrite; the hydrogen iodide is oxidised by the nitrous acid, and the liberated iodine may be expelled by boiling the solution. The solution is then neutralised with sodium carbonate and treated with *dilute* nitric acid; the hydrogen bromide is thus oxidised, and the bromine may be expelled by boiling the solution. The treatment with dilute nitric acid having been continued until no more bromine is evolved, the solution then contains the chloride, from which the chlorine may be obtained by the usual methods.

Some compounds formed by the union of two of the halogen elements are known, but they are not of much importance. When chlorine is passed over melted iodine in absence of moisture, **iodine monochloride,** ICl, distils, and condenses to a reddish-brown liquid which crystallises when it is cooled. The monochloride combines directly with chlorine, giving **iodine trichloride,** ICl_3, an orange crystalline solid. The compounds IF_5, IBr, and $ClBr$ are also known.

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* It is customary, especially in reference to qualitative analysis, to speak of the separation of two or more *elements*, when what is really meant is the separation of some *compounds* of those elements. Thus if a solution containing silver nitrate and potassium nitrate is treated with sufficient hydrochloric acid to precipitate all the combined silver, and the silver chloride is then removed by filtration, the 'silver' and 'potassium' are said to have been separated from one another, although both metals are still in a combined form. Consequently in describing such separations it may be unnecessary to state how the free elements are obtained, the methods employed for such purposes having been given elsewhere.

CHAPTER XLVI.

The Oxides and Oxy-Acids of the Halogens.

None of the halogens combines directly with oxygen; but oxides of chlorine and of iodine may be obtained by indirect processes. Several important compounds containing chlorine, bromine, or iodine, combined with oxygen *and* hydrogen, are also known; these compounds are classed together as the **oxy-halogen acids.**

COMPOUNDS OF THE TYPE HOX OR $H-O-X$.

When chlorine is passed into a *cold* aqueous solution of potassium hydroxide (p. 677) the gas is rapidly absorbed and the potassium salt of *hypochlorous acid* is formed, together with potassium chloride and water,

$$Cl_2 + 2KOH = KOCl + KCl + H_2O.$$

The solution has bleaching properties, especially when it is acidified, and as long ago as 1785 such a solution was prepared by Berthollet at Javelle for bleaching on a large scale.

The solution was known as '*Eau de Javelle*,' and was actually obtained by using crude potashes (potassium carbonate, p. 276) instead of potassium hydroxide; the results are not quite the same as when potassium hydroxide is used (p. 430).

When bromine is dropped into a *cold* aqueous solution of potassium hydroxide the colour of the halogen immediately disappears, and the two salts, potassium bromide and *potassium hypobromite*, remain in solution,

$$Br_2 + 2KOH = KBr + KOBr + H_2O.$$

In like manner iodine dissolves in potassium hydroxide solution, giving potassium iodide and *potassium hypoiodite*, KIO.

Calcium hydroxide, barium hydroxide, and other similar basic hydroxides also act on chlorine in the same way as do potassium hydroxide and sodium hydroxide,* a chloride and a hypochlorite being formed,

$$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

Corresponding compounds of bromine and of iodine are formed in a similar manner.

In preparing a hypochlorite, hypobromite, or hypoiodite, the solution must be kept *cold* (p. 432).

When a feebly basic metallic oxide (such as mercuric oxide) or hydroxide, or a carbonate, is suspended or dissolved in water and a halogen is added to the liquid, reactions occur similar to those described above; but only the salt of the halogen acid is formed, the oxy-halogen acid remaining free. It is possible to account for this result by assuming that the first change under these conditions is the formation of the two acids,

$$Cl_2 + H_2O = HCl + HOCl.$$

The hydrochloric acid then acts on the oxide, hydroxide, or carbonate (forming a chloride), but the hypochlorous acid, which is a very weak acid (see below), does not, and remains in the free state. The final result may therefore be expressed by an equation such as,

$$2Cl_2 + HgO + H_2O = HgCl_2 + 2HOCl.$$

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* Sodium hydroxide and potassium hydroxide are so similar in properties that for most purposes it makes little difference which is used, except, of course, that the one gives sodium, the other potassium derivatives.

Hypochlorous acid, $HOCl$, is obtained in aqueous solution when the solution of calcium hypochlorite prepared as indicated above (or a solution of bleaching powder, p. 639) is cautiously treated with very dilute (5 per cent.) nitric acid and then distilled,

$$Ca(OCl)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HOCl.$$

The quantity of nitric acid used must be less than that required to decompose all the calcium hypochlorite, otherwise some hydrochloric acid is liberated from the calcium chloride present, and some of the hypochlorous acid is then immediately decomposed,

$$HCl + HOCl = Cl_2 + H_2O.$$

The aqueous distillate has a yellow colour and a peculiar, disagreeable smell.

Hypochlorous acid is unstable, and it decomposes slowly even when its aqueous solution is kept in the dark, but much more rapidly in direct sunlight; in the former case it gives principally chloric and hydrochloric acids,

$$3HOCl = HClO_3 + 2HCl;$$

but in the latter it gives principally hydrochloric acid and oxygen,

$$2HOCl = 2HCl + O_2.$$

As chloric and hydrochloric acids react, giving chlorine (p. 431), this gas is also evolved from concentrated solutions of hypochlorous acid, especially when they are warmed.

Hypochlorous acid is only a very feeble acid, and it is liberated from its salts even by carbonic acid; many of its salts are readily hydrolysed (p. 361). The acid is a vigorous oxidising agent; its aqueous solution oxidises hydrogen chloride, giving chlorine (see above); ammonia, giving nitrogen; and hydrogen sulphide, giving sulphur. Hydrogen chloride and water are also formed in the last two cases,

$$2NH_3 + 3HOCl = N_2 + 3H_2O + 3HCl$$
$$SH_2 + HOCl = S + H_2O + HCl.$$

Hypochlorous acid bleaches litmus, indigo, and many other coloured carbon compounds. As the acid is readily liberated from hypochlorites, the latter (calcium hypochlorite, sodium hypochlorite) are used in bleaching on the commercial scale.

Hypochlorites are formed, together with chlorides, when an aqueous solution of a chloride such as sodium chloride is submitted to electrolysis, provided that the solution is kept *cold* and well stirred during the operation; under these conditions the chlorine which is set free at the positive electrode is not liberated as a gas, but is acted on by the sodium hydroxide which is formed at the negative electrode (p. 303).

Hypobromous acid, $HOBr$, is similar to hypochlorous acid in properties. The existence of hypoiodous acid, HOI, is doubtful.

Chlorine monoxide, Cl_2O, is formed when pure dry chlorine is passed over mercuric oxide which is kept at 0°,

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

It is a yellowish-brown gas, having an irritating smell, and it oxidises many substances with explosive violence; it dissolves in water, giving hypochlorous acid, for which reason it is regarded as the *anhydride* (p. 233) of this acid,

$$Cl_2O + H_2O = 2HOCl.$$

COMPOUNDS OF THE TYPE HXO_3 OR $H-O-XO_2$.

When an aqueous solution of a hypochlorite is evaporated, even at ordinary temperatures, some of the hypochlorite is converted into chloride and *chlorate*; the same change occurs, but more rapidly and completely, when the solution is heated,

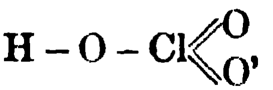
$$3KOCl = 2KCl + KClO_3$$
$$3Ca(ClO)_2 = 2CaCl_2 + Ca(ClO_3)_2.$$

Hence on chlorine being passed into a *hot* solution of potassium hydroxide, sodium hydroxide, barium hydroxide, &c., instead of a hypochlorite and a chloride, a chlorate and a chloride are formed. The final result of the two reactions, which occur successively, and which are expressed respectively by the equations already given, may be summarised as follows,

$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O$$
$$6Cl_2 + 6Ca(OH)_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

As the chlorates are generally far less soluble in cold water than the corresponding chlorides, the former may often be obtained in a state of purity by evaporating the solution, removing the crystals which are first deposited from the cold solution, and then purifying them by recrystallisation from water. *Bromates* and *iodates* may be prepared by similar methods.

Since the chlorates, bromates, and iodates of sodium and potassium are decomposed at a red heat, giving the corresponding chloride, bromide, or iodide, the preparation of one of these halides from the *element* is accomplished by dissolving the halogen in approximately the theoretical quantity of a solution of sodium or potassium hydroxide, and then evaporating the solution to dryness and strongly igniting the residue. The halide thus obtained is then purified by recrystallisation from water.

Chloric acid, $HClO_3$ or  $H-O-Cl\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$, is obtained in aqueous solution when barium chlorate is treated with a dilute solution of an equivalent quantity of sulphuric acid and the precipitated barium sulphate is separated by filtration through asbestos,

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4.$$

On the solution being evaporated below 40° under reduced pressure, a colourless, odourless, concentrated solution of the acid remains.*

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* The principle illustrated here is very often used in preparing acids which decompose when they are heated or which are not volatile. By using exactly the right proportion of sulphuric acid the whole of the barium is precipitated as the insoluble sulphate, and the filtered solution contains only the desired acid. Similarly, soluble silver salts may be decomposed with the equivalent quantity of hydrochloric acid, soluble lead salts with hydrogen sulphide, and so on.

Chloric acid decomposes when its concentrated solution is heated, giving perchloric acid, water, and chlorine dioxide (or oxygen and chlorine),

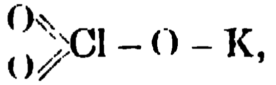
$$3HClO_3 = HClO_4 + H_2O + 2ClO_2.$$

It is a vigorous oxidising agent, and oxidises hydrogen chloride, for example, giving water and chlorine,

$$HClO_3 + 5HCl = 3H_2O + 3Cl_2.$$

The salts of chloric acid, of which potassium chlorate is the most important, are prepared on the large scale for use as oxidising agents.

Solutions of chlorates, unless very concentrated, do not give a precipitate with silver nitrate, because silver chlorate is *soluble* in water. When a chlorate is warmed with concentrated sulphuric acid, chloric acid is liberated, but is immediately decomposed (see above); the chlorine dioxide thus formed explodes violently, so that the reaction should be performed with very small quantities (say 0·1 gram) only.

Potassium chlorate, $KClO_3$ or  $\begin{matrix}O\\O\end{matrix}\!\!>\!Cl-O-K$, is prepared in the laboratory by passing chlorine into a hot solution of potassium hydroxide (or potassium carbonate) until the gas is no longer absorbed; the solution is then concentrated, and the potassium chlorate which separates on cooling (leaving the chloride in the mother-liquor) is recrystallised from boiling water.

It is prepared on the large scale by first saturating hot 'milk of lime' with chlorine; the solution of calcium chlorate and chloride thus obtained is treated with potassium chloride (p. 404), evaporated, and allowed to cool. As the potassium chlorate formed by the reversible reaction,

$$Ca(ClO_3)_2 + 2KCl \longleftrightarrow 2KClO_3 + CaCl_2,$$

is only sparingly soluble in cold water and is deposited in crystals as the solution cools, the reaction proceeds from left to right until most of the calcium chlorate has been decomposed. The product is purified by recrystallisation.

Potassium chlorate is also manufactured by the electrolysis of a *hot* solution of potassium chloride (platinum-iridium anodes and iron-nickel cathodes being used). The potassium hypochlorite formed as a secondary product of electrolysis is thus converted into the chlorate and chloride, and the former is obtained in crystals by concentrating and then cooling the solution. Other chlorates are prepared in a similar manner.

Potassium chlorate melts at about 360°, and begins to decompose with appreciable rapidity at a slightly higher temperature (p. 82). Owing to its relative instability and the large proportion of oxygen liberated by its decomposition, it is a very vigorous oxidising agent at high temperatures and under other conditions as well. Thus when a little potassium chlorate is thrown on red-hot charcoal a vigorous *deflagration* ensues, and when a mixture of potassium chlorate and sulphur, or potassium chlorate and cane-sugar, is struck with a hammer on an anvil, a violent explosion occurs.*

Potassium chlorate is often used in the laboratory as an oxidising agent in conjunction with hydrochloric acid, which first liberates from it chloric acid; in such cases the oxidising action is due to the chlorine which is set free by the interaction of the chloric and hydrochloric acids (p. 434). It is also used in the manufacture of matches and fireworks.

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* It is obvious that these mixtures must *not* be made by grinding their components together, otherwise dangerous explosions will result. They are prepared by carefully mixing the finely ground components (about 1 part of sugar or 2 parts of sulphur to 4 parts of chlorate) on a piece of paper with a horn spatula, and, particularly in the case of sulphur and potassium chlorate, small quantities only (say 0·5 gram) of the mixture should be prepared and used. The mixture of sugar and chlorate is safe to handle, and may be prepared (but not exploded) in larger quantities (say 10 grams); this mixture may also be inflamed by touching it with a glass rod which is moistened with concentrated sulphuric acid.

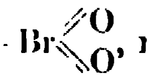
Chlorine dioxide, ClO_2, formed in the manner mentioned above (p. 434), is a dark, greenish-yellow gas which explodes when it is heated, giving oxygen and chlorine. It combines with water, yielding a mixture of chlorous and chloric acids,

$$2ClO_2 + H_2O = HClO_2 + HClO_3,$$

and with potassium hydroxide, giving a mixture of *chlorite* and chlorate.

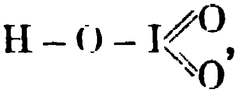
Chlorous acid, $HClO_2$ or $H-O-ClO$, is only known in the form of its salts (the *chlorites*), and even these undergo decomposition in aqueous solution, with production of a chlorate and a chloride,

$$3KClO_2 = 2KClO_3 + KCl.$$



Bromic acid, $HBrO_3$ or $H-O-Br\genfrac{}{}{0pt}{}{/\!\!/O}{\backslash\!\!\backslash O}$, may be prepared in solution by methods similar to those used in the case of chloric acid, which it resembles in properties. When treated with iodine it gives iodic acid, and bromine is set free,

$$2HBrO_3 + I_2 = 2HIO_3 + Br_2.$$



Iodic acid, HIO_3 or $H-O-I\genfrac{}{}{0pt}{}{/\!\!/O}{\backslash\!\!\backslash O}$, occurs as a salt in caliche (p. 414), and may be obtained in various ways. In the form of a salt it is produced by treating iodine with a hot aqueous solution of potassium hydroxide, barium hydroxide, &c.; the very unstable hypoiodite which is first formed (p. 430) is converted into iodate and iodide (p. 432), so that the final result is expressed by an equation such as,

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O.$$

Free iodic acid is prepared by passing chlorine into water which contains iodine in suspension and in solution,

$$5Cl_2 + 6H_2O + I_2 = 2HIO_3 + 10HCl.$$

As iodic acid oxidises hydrogen chloride in strong solutions, plenty of water must be used, and the hydrogen chloride must be precipitated with silver oxide before the solution is concentrated.

A better method is to warm finely powdered iodine with a large quantity of concentrated nitric acid until no free iodine remains; on the solution being evaporated, iodic acid is obtained in colourless crystals, which are purified by re-crystallisation from water,

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O.$$

Iodic acid is a fairly stable compound, but when heated at 170° it decomposes into water and its anhydride, I_2O_5. It is a vigorous oxidising agent, and is rapidly reduced by many compounds. Thus when treated with sulphurous acid (or an acid sulphite, p. 414), with hydrogen sulphide, or with hydrochloric acid, it gives a precipitate of iodine.

The first change in these reductions probably results in the formation of hydrogen iodide, and may be represented by a partial equation such as,

$$HIO_3 + 3H_2SO_3 = 3H_2SO_4 + HI.$$

The hydriodic acid then acts on some of the iodic acid,

$$5HI + HIO_3 = 3H_2O + 3I_2,$$

so that the final result may be expressed by

$$2HIO_3 + 5H_2SO_3 = 5H_2SO_4 + I_2 + H_2O.*$$

To look at the matter in another way: $2HIO_3 = H_2O + I_2O_5$, so that two molecules of iodic acid give, when reduced to iodine, 5 atoms of oxygen, which will oxidise $5SO_2$ to $5SO_3$, $5H_2S$ to $5H_2O$ and sulphur, and so on. If the reducing agent is added in greater proportion, the liberated iodine may be converted into hydrogen iodide (p. 415).

There is some uncertainty as to whether the molecular formula of iodic acid is HIO_3 or $H_2I_2O_6$ or $H_3I_3O_9$, as salts are known of the composition MHI_2O_6 and $MH_2I_3O_9$, as well as MIO_3, where M represents 1 atom of a univalent metal.

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* This equation is deduced in the following manner: The quantities represented in the first partial equation are multiplied by 5 in order to obtain the 5HI required in the second partial equation. By combining the two partial equations, the expression

$$6HIO_3 + 15H_2SO_3 = 15H_2SO_4 + 3H_2O + 3I_2$$

is then obtained, and the quantities here represented are finally divided by 3 for the sake of simplicity.

Silver iodate, $AgIO_3$, is a colourless crystalline substance, practically insoluble in water. **Iodic anhydride**, I_2O_5, is a colourless solid which combines with water, giving iodic acid; it decomposes into its elements at about 300°. **Iodine dioxide**, IO_2 or I_2O_4, is a lemon-yellow solid, obtained by cautiously heating iodic acid with concentrated sulphuric acid.

COMPOUNDS OF THE TYPE HXO_4 OR $H-O-XO_3$.

When potassium chlorate is heated gradually, it melts and then decomposes, giving oxygen, potassium chloride, and *potassium perchlorate*,

$$2KClO_3 = O_2 + KCl + KClO_4.$$

If the heating is discontinued as soon as the melted mass becomes pasty (while kept at about the same temperature), and the residue is then cooled and treated with boiling hydrochloric acid (to decompose any unchanged chlorate), most of the potassium chloride dissolves, and the remaining sparingly soluble perchlorate may be purified by recrystallisation from boiling water.

Perchloric acid, $HClO_4$, is obtained when potassium perchlorate is distilled with sulphuric acid under reduced pressure.

It is also formed when chlorates are treated with sulphuric acid, the liberated chloric acid decomposing in the manner already described (p. 431).

Perchloric acid is a colourless, extremely dangerous liquid. Although stable in aqueous solution, the acid itself decomposes spontaneously even in the dark, often with explosive violence. It also explodes when it is brought into contact with wood, paper, and similar substances, on which it acts as an oxidising agent. On the other hand, in cold aqueous solution it does not oxidise hydrogen chloride,* hydrogen sulphide, or sulphurous acid. When treated with iodine it yields iodic acid (p. 436).

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* The difference in behaviour between a chlorate and a perchlorate towards hydrochloric acid may be utilised in estimating the former in presence of the latter.

Chlorine heptoxide, Cl_2O_7 (or *perchloric anhydride*), is obtained when perchloric acid is cautiously treated with phosphoric anhydride, and the mixture is then distilled. It is a liquid boiling at 82°, and is explosive; it combines with water, giving perchloric acid.

Periodic acid is obtained as a salt when chlorine is passed into a hot aqueous solution of sodium iodate and sodium hydroxide; the sodium hydroxide gives rise to sodium hypochlorite, and the latter oxidises the iodate to periodate.

The free acid, $HIO_4, 2H_2O$ or H_5IO_6, may be obtained by the electrolytic oxidation of a solution of iodic acid. It is crystalline, and decomposes at 140°, giving iodine, oxygen, and water. Its aqueous solution oxidises hydrogen iodide, giving iodine; when treated with sulphurous acid it is first reduced to iodic acid and then to hydriodic acid, which then react, giving iodine, when a certain proportion of the reducing agent has been added.

A compound of the composition HIO_4, corresponding with $HClO_4$, has not been isolated, although salts such as $AgIO_4$ and $NaIO_4$ are known. The composition of the free acid is H_5IO_6, which corresponds with $HIO_4 + 2H_2O$, but for certain reasons free periodic acid is not regarded as HIO_4 crystallised with two molecules of water.* It is more probably a pentabasic acid, $IO(OH)_5$, which, however, generally acts as a dibasic acid, and forms acid salts of the type $Na_2H_3IO_6$ or $IO(OH)_3(ONa)_2$. Many different acid or hydrogen salts derived from this acid are known, and also many salts derived from other closely related compounds, such as H_3IO_5 or $IO_2(OH)_3$.

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* When one molecule of H_5IO_6 is treated with one molecule of potassium hydroxide the heat of neutralisation is only 5150 calories; with two and three molecules of the hydroxide the heats of neutralisation are 26,590 and 29,740 calories respectively. Since the heat of neutralisation for the proportion $H_5IO_6 : 2KOH$ is so very much greater than for $H_5IO_6 : KOH$, and since the value for the former is very little less than for the proportion $H_5IO_6 : 3KOH$, it would seem that the acid is dibasic.

THE VALENCY OF THE HALOGENS IN THEIR OXYGEN COMPOUNDS.

The oxy-halogen acids which have now been described or mentioned are monobasic (except certain periodic acids), and belong to one of the following types, where X represents one atom of a halogen:

HXO (H-O-X).	HXO_2.	HXO_3.	HXO_4.
Hypochlorous acid.	Chlorous acid.	**Chloric acid.**	**Perchloric acid.**
Hypobromous acid.	—	Bromic acid.	—
Hypoiodous acid.	—	**Iodic acid.**	Periodic acid.

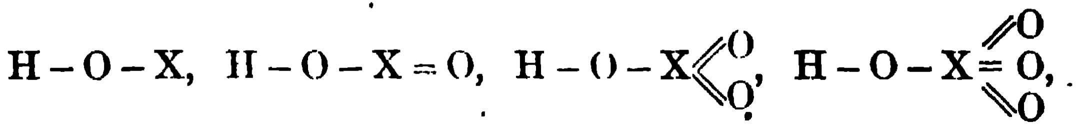
The names of the more important compounds are printed in heavy type.

It will be seen from this table, and from the description which has been given of these compounds, that the close relationship already observed between the members of the halogen family (p. 423) is also exhibited in their oxides and oxy-acids; broadly speaking, the three elements which give rise to such compounds form corresponding derivatives identical in type.

Now it would be possible to assume that the halogens are univalent in these oxy-acids and in their oxides, just as they are in their compounds with hydrogen and the metals. Thus the different types of acids might conceivably be represented by the structural formulæ,

$$H-O-X, \quad H-O-O-X, \quad H-O-O-O-X,$$
$$\text{and } H-O-O-O-O-X$$

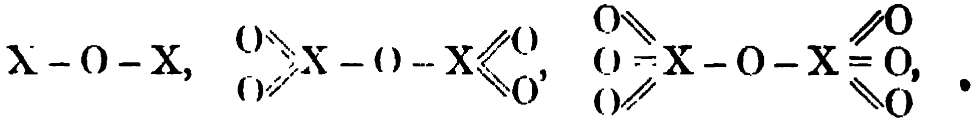
respectively. But from an examination of the properties of the elements as a whole, it must be concluded that the valency of an element may vary; that this property depends on the nature of the other element or elements with which the given element is combined. A general rule in this connection is that the valency of an element towards hydrogen and other electro-positive (p. 390) elements is different from its valency towards oxygen and other electro-negative elements. Thus in the case of the oxy-halogen acids it would seem that their structures should be represented respectively by the following formulæ,



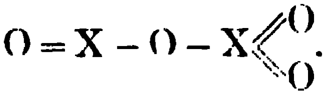
$$H-O-X,\quad H-O-X=O,\quad H-O-X\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix},\quad H-O-X\begin{smallmatrix}\diagup\!\!\diagup O\\ = O,\\ \diagdown\!\!\diagdown O\end{smallmatrix}$$

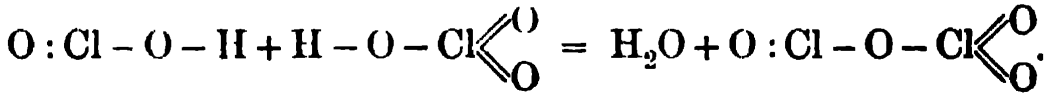
in which the valency of the halogen is 1, 3, 5, and 7 respectively, but the evidence in favour of these formulæ is not very conclusive.

The structures of the anhydrides of the types X_2O, X_2O_5, and X_2O_7 would then be expressed respectively by the corresponding formulæ,



$$X-O-X,\quad \begin{smallmatrix}O\diagdown\!\!\diagdown\\ O\diagup\!\!\diagup\end{smallmatrix}X-O-X\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix},\quad \begin{smallmatrix}O\diagdown\!\!\diagdown\\ O=\\ O\diagup\!\!\diagup\end{smallmatrix}X-O-X\begin{smallmatrix}\diagup\!\!\diagup O\\ = O,\\ \diagdown\!\!\diagdown O\end{smallmatrix}$$

which would indicate their relationships to the acids, while the oxides X_2O_4 would be represented by the formula  $O=X-O-X\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix}$. Although the vapour density of chlorine dioxide corresponds with the simple formula ClO_2, it may be supposed that these molecules are dissociation products of Cl_2O_4 (compare N_2O_4, p. 350). This view seems to be borne out by the behaviour of the oxide towards water (p. 436); since it gives a mixture of chlorous and chloric acids, it is probably a *mixed anhydride*, that is to say, an anhydride derived from two *different* molecules,



$$O:Cl-O-H+H-O-Cl\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix} = H_2O+O:Cl-O-Cl\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix}.$$

CHEMICAL NOMENCLATURE.

Although the names of chemical compounds are not always chosen in accordance with a definite system, certain general rules are observed in the case of acids and of the salts derived from them.

When the hydrogen compound of an element is an acid, its name is derived from those of the two elements contained in it, as in the case of hydrogen chloride and the other halogen acids. The aqueous solution of the compound, and often also the compound itself, are also denoted by applying the prefix *hydro* and the suffix *ic* to the name of the non-metallic or electro-negative element, or to an abbreviation of this name. Thus an aqueous solution of hydrogen chloride is called *hydro*chlor*ic* acid. The salts derived from such acids (which do not contain oxygen) are simply named after the two elements which they contain, the termination *ide* being used with the name of the electro-negative element, as, for example, sodium chlor*ide*, calcium fluor*ide*.

When elements form acids which contain oxygen, the names of these acids are derived from those of the distinctive acid-forming element. Thus the compound H_2SO_4 is called sulphuric acid because it is derived from the acid-forming oxide or anhydride of the element sulphur; the compound H_3PO_4 is called phosphoric acid because it is derived from an oxide of phosphorus The salts of such acids which contain oxygen have names ending in *ate*. In many cases, however, a given element forms two acids containing oxygen; the name of the acid corresponding with the *lower* oxide then ends in *ous*, and the salts derived from it in *ite*. Thus the oxides SO_2 and SO_3 give rise to the acids H_2SO_3 and H_2SO_4 respectively; the compound H_2SO_3 is therefore named sulphur*ous* acid, and its salts are termed sulph*ites*.

If more than two oxygen acids are derived from a given element, the prefix *hypo* is used to denote a *lower* stage of oxidation than the *ous* acid, and the prefix *per* to denote a *higher* stage of oxidation than the *ic* acid. Thus to distinguish them from chlorous acid, $HClO_2$, and chloric acid, $HClO_3$, the compounds $HClO$ and $HClO_4$ are named *hypo*chlorous and *per*chloric acid respectively

CHAPTER XLVII.

Manganese and its Compounds.

MANGANESE, Mn.;* AT. WT. 54·9.

The black crystalline mineral pyrolusite, which is used as an oxidising agent in preparing the halogens (pp. 140, 409), consists principally of manganese dioxide, MnO_2, and is the chief source of all commercial manganese compounds.† Several other oxides of manganese occur in nature, and most iron ores contain manganese compounds, but manganese is not found in the free state.

Manganese is a metal (p. 255), and, like a great many other metals, it may be obtained by reducing its oxides with carbon (coal, charcoal), but an extremely high temperature is required to bring about reduction.

It may be prepared in the laboratory by reducing manganese dioxide with aluminium,‡

$$3MnO_2 + 4Al = 3Mn + 2Al_2O_3.$$

A small quantity (say 20 g.) of a mixture of *dried* manganese dioxide and dried aluminium powder (free from grease) is placed in a small crucible, the end of a short piece of magnesium ribbon is pushed into the mixture, and the magnesium is ignited. As soon as the very vigorous reaction is at an end, a further quantity of the mixture is added, and the addition is repeated at suitable intervals if required. In consequence of the great heat development both the manganese and the aluminium oxide are melted, and the two liquids separate, the oxide rising to the top; if a slight excess of manganese dioxide is used, the manganese is free from aluminium. This process was discovered by Goldschmidt, who also used aluminium for the reduction of several other metallic oxides (pp. 502, 704).

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* The molecular formulæ of many of the metals are unknown; in such cases the molecule is represented by the atom of the element.

† Pyrolusite generally contains silica and carbonates of barium, calcium, iron, and manganese.

‡ In this and in similar experiments the eyes should be protected, as the reaction is extremely violent and may possibly be explosive.

Manganese is little used alone, but its alloys are commercially important. It rusts in the atmosphere and is readily attacked by dilute hydrochloric or sulphuric acid, giving manganous salts and liberating hydrogen.

THE MANGANOUS COMPOUNDS.

When manganese dioxide is heated with excess of concentrated hydrochloric acid until the evolution of chlorine ceases and the (filtered) solution is then evaporated and cooled, a pink, crystalline, readily soluble salt, **manganous chloride,** $MnCl_2 + 4H_2O$, is obtained.

This salt is not derived from, and does not correspond with, manganese dioxide (p. 286). It is a derivative of mangan*ous* oxide, MnO, because the metal has the same valency in this oxide as in manganous chloride.

Now a metallic oxide which gives rise to corresponding salts is termed a *basic oxide;* mangan*ous* oxide, therefore, is a basic oxide, and the salts derived from it are called the mangan*ous* salts.

A solution of manganous chloride when treated with sodium hydroxide solution (in absence of air) gives a colourless, flocculent precipitate of **manganous hydroxide,**

$$MnCl_2 + 2NaOH = Mn(OH)_2 + 2NaCl.$$

This hydroxide is insoluble in water, but it dissolves chemically in acids, giving the corresponding salts.

Manganous hydroxide is *not* precipitated from a solution of a manganous salt by sodium hydroxide if the solution also contains excess of ammonium chloride or other ammonium salts, in which manganous hydroxide is chemically soluble.*

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* Nearly all the metallic hydroxides of the type $X(OH)_2$ which are insoluble in water dissolve chemically in solutions of ammonium salts (p. 621).

Manganous hydroxide, like most metallic hydroxides, is readily decomposed when it is heated, giving **manganous oxide,** MnO, and water; in absence of air the oxide is obtained as a green powder, which combines with oxygen very readily.

Manganous carbonate, $MnCO_3$, is obtained as a colourless precipitate when a manganous salt is treated with sodium carbonate in aqueous solution. It is insoluble in water, but it dissolves chemically in acids, giving manganous salts, and it decomposes when it is heated, giving manganous oxide and carbon dioxide; these are properties common to the *normal* carbonates of most of the metals (p. 276).

Manganous sulphate, $MnSO_4$, may be prepared by dissolving the hydroxide or the carbonate in sulphuric acid and then evaporating the solution; at low temperatures it separates in pink hydrated crystals, which have the composition $MnSO_4, 7H_2O$.

Manganous sulphide, MnS, is formed as a flesh-coloured precipitate on ammonium sulphide being added (p. 267) to a manganous salt in aqueous solution. It is insoluble in water, but it dissolves chemically in strong acids, giving hydrogen sulphide and a manganous salt.

MANGANESE DIOXIDE AND THE MANGANITES.

Although all elements which are classed as metals form at least *one* basic oxide, many metals also form acidic oxides (anhydrides), and, from the latter, acids are produced either by direct combination with water or by indirect processes. This is the case with the metal manganese; manganese dioxide may be regarded as the anhydride of a dibasic acid, *manganous acid*, $H_2MnO_3(MnO_2 + H_2O)$, or of a tetrabasic acid, *orthomanganous acid*, $H_4MnO_4(MnO_2 + 2H_2O)$, although neither of these compounds has been obtained in a pure state.

When manganous hydroxide, prepared as described above, is merely exposed to the air in a moist state, it gradually darkens in colour and ultimately becomes black. This is the result of atmospheric oxidation, but as the product cannot be purified and as different preparations differ in composition, it is not known exactly what is formed. It seems probable, however, that the black substance contains manganous acid,

$$2Mn(OH)_2 + O_2 = 2H_2MnO_3.$$

Manganous acid may be obtained as a black precipitate, mixed with sodium manganite, by adding sodium hydroxide and sodium hypochlorite or sodium hypobromite (or sodium hydroxide and then chlorine- or bromine-water, p. 429) to a solution of a manganese salt,

$$Mn(OH)_2 + NaOCl = H_2MnO_3 + NaCl.$$

The (impure) substance which is formed in this and in several other ways described later (p. 449) is generally called '*hydrated manganese dioxide*,' as its composition is represented approximately by the formula MnO_2, H_2O.

Manganese dioxide, MnO_2 or $O=Mn=O$, remains as a black powder when this hydrated substance is washed with water, dried, and gently heated. The dioxide yields oxygen when it is strongly heated alone or with concentrated sulphuric acid,

$$3MnO_2 = Mn_3O_4 + O_2$$
$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Manganese dioxide is used in the preparation of the halogens, the permanganates, and other salts, some of which are employed in dyeing; it is also utilised in the manufacture of glass.

When a little manganese dioxide is melted with a colourless glass (p. 293), the product has an amethystine colour. Glass made from materials which contain ferrous compounds has a greenish or greenish-yellow tinge (bottle-glass), but when a little manganese dioxide is also used, the resulting glass is practically colourless, because amethyst and green are complementary colours. It may be, also, that the green ferrous compounds are oxidised to ferric compounds, which have hardly any colour and impart only an almost imperceptible yellow tinge to the glass.

Salts of manganous acid, like the acid itself, are unknown in a pure state, but certain impure manganites are utilised commercially in **Weldon's process** for the recovery of the manganese dioxide which has been used in preparing chlorine.

In this process the liquors from the chlorine generators are first neutralised with limestone, which at the same time causes the precipitation of ferric hydrate.* The clear solution of manganous chloride is now mixed with milk of lime in suitable proportion, whereby manganous hydroxide is precipitated; the whole is then heated to 55°, and a stream of air is blown through the liquor. In this way manganous acid is formed by the oxidation of the manganous hydroxide, and a black precipitate of impure *calcium manganite*, $CaMnO_3$, is obtained; after the precipitate is allowed to settle, the liquor is run off. The *residue* is used in preparing chlorine, since with hydrochloric acid it first gives calcium chloride and hydrated manganese dioxide (manganous acid), and the latter then behaves like manganese dioxide.

A compound of the composition, Mn_3O_4, occurs in nature as a mineral (*hausmannite*), and is obtained as a red or brown powder by strongly heating manganous oxide in the air. It is also formed when manganese dioxide is very strongly heated, oxygen being evolved (p. 446).

When treated with acids this oxide does not yield corresponding salts, but behaves as if it were a mixture or a compound of $2MnO$ and MnO_2. With nitric acid, for example, it gives a manganous salt (2 molecules), with separation of manganese dioxide (1 molecule),

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O,$$

whereas with hot concentrated hydrochloric acid it gives a manganous salt, with evolution of chlorine,

$$Mn_3O_4 + 8HCl = 3MnCl_2 + Cl_2 + 4H_2O.$$

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* Ferric chloride is decomposed by calcium carbonate, but ferric carbonate is not obtained because it is immediately hydrolysed by water.

$$2FeCl_3 + 3CaCO_3 = Fe_2(CO_3)_3 + 3CaCl_2$$
$$Fe_2(CO_3)_3 + 6H_2O \longleftrightarrow 2Fe(OH)_3 + 3H_2CO_3.$$

From this behaviour it may be inferred that the compound is the mangan*ous* salt, Mn_2MnO_4, of orthomanganous acid, $Mn(OH)_4$ or H_4MnO_4 (compare p. 445).

An oxide of the composition, Mn_2O_3, occurs in nature as a mineral (*braunite*), and is obtained as a dark-brown powder, commonly known as manganese sesquioxide, when manganous oxide or manganese dioxide is *gently* heated in the air. Towards dilute sulphuric and nitric acids it behaves as if it were a mixture or compound of MnO and MnO_2, so that it might be regarded as a manganese salt, $MnMnO_3$, derived from manganous acid, $MnO(OH)_2$ or H_2MnO_3. On the other hand, with concentrated sulphuric acid it gives the *corresponding* salt, manganic sulphate,

$$Mn_2O_3 + 3H_2SO_4 = Mn_2(SO_4)_3 + 3H_2O,$$

and in this case behaves like a basic oxide.

Now the oxides of iron and of chromium of the type X_2O_3 are basic oxides, and the corresponding hydroxides, sulphates, chlorides, &c. are well-known compounds; from analogy, therefore, the compound Mn_2O_3 might well be regarded as a basic oxide. Whatever may be the nature of this compound, certain salts derived from an oxide of this type are known, and are termed *manganic salts;* they are, however, very unstable, and are hydrolysed by water.

Manganic sulphate, $Mn_2(SO_4)_3$, is also obtained by gently heating manganese dioxide with sulphuric acid,

$$4MnO_2 + 6H_2SO_4 = 2Mn_2(SO_4)_3 + 6H_2O + O_2;$$

it is a dark-green, deliquescent substance.

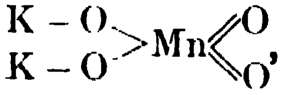
Manganic chloride, $MnCl_3$, is possibly contained in the dark-brown solution which results when manganese dioxide is treated with concentrated hydrochloric acid at low temperatures; the tetrachloride, $MnCl_4$, may also be present in this liquid.

Manganic hydroxide, $MnO(OH)$, occurs as a mineral (*manganite*), and is formed when manganic sulphate is treated with water,

$$Mn_2(SO_4)_3 + 6H_2O = 3H_2SO_4 + 2Mn(OH)_3,$$
$$2Mn(OH)_3 = 2MnO(OH) + 2H_2O;$$

it dissolves in hot sulphuric acid, giving manganic sulphate.

MANGANATES AND PERMANGANATES.

Potassium manganate, K_2MnO_4 or  $\begin{matrix}K-O\\K-O\end{matrix}\!>\!Mn\!\begin{matrix}\diagup O\\\diagdown O\end{matrix}$, is obtained as a green mass when manganese dioxide is heated with potassium hydroxide in presence of (atmospheric) oxygen, or, better, in presence of some potassium chlorate or potassium nitrate, or any salt which gives oxygen when it is heated.

The same substance is formed when any other oxide, or any salt of manganese, is treated in this way,

$$MnO_2 + 2KOH + O = K_2MnO_4 + H_2O.*$$

When suitable proportions of dioxide, chlorate, and potassium hydroxide are used, the product may be obtained in crystals by dissolving it in a small quantity of water, and then allowing the solution to evaporate at ordinary temperatures.

Potassium manganate dissolves in a relatively small quantity of water, giving a beautiful green solution; but on this solution being *diluted* largely with water it turns pink, owing to the formation of potassium permanganate, and a precipitate of hydrated manganese dioxide (p. 446) is formed,

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO_2, H_2O + 4KOH.$$

The conversion of the manganate into the permanganate may also be brought about by adding an acid, or some oxidising agent, without diluting the solution.

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* In this and in many other partial equations the proportion of an element may be expressed in *atoms* instead of in molecules in cases where the element in question reacts in the nascent state (p. 340). The oxygen represented in this equation is not (atmospheric) molecular oxygen, but that derived from potassium chlorate or nitrate.

Potassium manganate is hydrolysed by water: the manganic acid, which, presumably, is formed, then decomposes, giving a precipitate of hydrated manganese dioxide and permanganic acid; this acid reacts with the potassium hydroxide, forming the potassium salt and water. These changes,

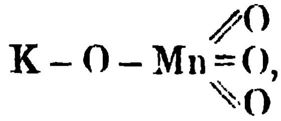
$$K_2MnO_4 + 2H_2O = H_2MnO_4 + 2KOH,$$
$$3H_2MnO_4 = 2HMnO_4 + MnO_2, H_2O + H_2O,$$

and the formation of the potassium permanganate from the permanganic acid, are summarised in the equation (p. 449). Potassium manganate dissolves in a concentrated solution of potassium hydroxide or sodium hydroxide without undergoing decomposition, as the great concentration of the alkali prevents hydrolysis, and the salt is much more stable than the acid.

Sodium manganate, Na_2MnO_4, is easily obtained by using sodium hydroxide in place of potassium hydroxide in the reactions described above, and also by heating manganese dioxide with sodium peroxide (p. 671),

$$MnO_2 + Na_2O_2 = Na_2MnO_4.$$

Other manganese compounds also yield sodium manganate under these conditions.

Potassium permanganate, $KMnO_4$ or  $K-O-Mn{\equiv}O_3$, is one of the most important manganese compounds, and is prepared on the large scale. For this purpose the manganate is first manufactured by heating manganese dioxide with potassium hydroxide and potassium chlorate in iron vessels. The crude product is dissolved in a *large* volume of water, the precipitate of hydrated manganese dioxide is allowed to settle, and the clear solution is then evaporated. The potassium permanganate, which is finally deposited in crystals, may be purified by recrystallisation from water; the potassium hydroxide in the original mother-liquors (equation,

p. 449) may be used for preparing further quantities of the manganate.

Instead of the manganate being dissolved in a large volume of water, its concentrated solutions may be treated with carbon dioxide, or oxidised with chlorine or with ozone,

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$
$$2K_2MnO_4 + O_3 + H_2O = 2KMnO_4 + 2KOH + O_2,$$

or they may be submitted to electrolysis; in the last case potassium permanganate and potassium hydroxide are obtained in solution and hydrogen is evolved,

$$2K_2MnO_4 + 2H_2O = 2KMnO_4 + 2KOH + H_2.$$

Potassium permanganate forms dark reddish-purple crystals which have a greenish lustre; it is not very soluble in water (its solubility is 4·3 at 10°), but its saturated solution is intensely coloured. The solid is readily decomposed when it is heated alone,

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$

and a violent explosion may occur when it is heated with *concentrated* sulphuric acid,*

$$4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2,$$

but it is not decomposed by boiling *dilute* sulphuric acid.

Potassium permanganate is a salt of *permanganic acid*, $HMnO_4$, a compound which is derived from an anhydride, Mn_2O_7,

$$Mn_2O_7 + H_2O = 2HMnO_4.$$

In presence of many substances which can combine with oxygen, this acid is rapidly reduced to lower oxides of manganese (MnO_2 or MnO); hence potassium permanganate is a very important oxidising agent.

When used as an oxidising agent in presence of *excess* of dilute sulphuric acid, the acid $HMnO_4$ (which corresponds with the oxide Mn_2O_7) is reduced to manganous oxide,

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* For this reason permanganates must not be brought into contact with the concentrated acid.

$$2KMnO_4 + H_2SO_4 = K_2SO_4 + 2HMnO_4$$
$$2HMnO_4 = 2MnO + H_2O + 5O.^{*}$$

The manganous oxide, however, reacts with the sulphuric acid present, forming manganous sulphate and water, so that the decomposition of the permanganate may be more fully represented by the *partial* equation,

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Five atoms of oxygen available for oxidising purposes (*available oxygen*) are thus liberated from *two molecules* of the permanganate.

The decomposition represented by this *partial* equation does *not* occur in aqueous solution unless there is also some reducing agent present to combine with the liberated oxygen; but many substances will do this. Thus on adding excess of sulphurous acid, hydrogen sulphide, nitrous acid, oxalic acid, or ferrous sulphate (or hydrogen peroxide, p. 476) to a solution of potassium permanganate (in presence of *dilute* sulphuric acid), the colour of the permanganate immediately disappears and the added substance is oxidised.

In order to express by equations the changes which occur in these cases, it must be remembered that 2 molecules of permanganate give 5 atoms of available oxygen (see above), and that 1 atom of oxygen is required for the oxidation of 1 molecule of sulphurous acid, hydrogen sulphide, nitrous acid, or oxalic acid respectively; consequently 5 atoms of oxygen oxidise 5 molecules of each of these compounds, as shown by the following partial equations,

$$5H_2SO_3 + 5O = 5H_2SO_4 \qquad 5H_2S + 5O = 5H_2O + 5S\,\dagger$$
$$5HNO_2 + 5O = 5HNO_3 \qquad 5H_2C_2O_4 + 5O = 10CO_2 + 5H_2O.$$

The final results, therefore, are summarised by combining one of these partial equations with that given above for the decomposition of the permanganate; thus in the case of sulphurous acid,

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* This is a partial equation; compare footnote, p. 449.

† Compare footnote, p. 421.

$$2KMnO_4 + 3H_2SO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5H_2SO_4,$$

or, since sulphuric acid is formed, and therefore need not be added originally,

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 3H_2O + 2H_2SO_4.$$

In the case of the oxidation of oxalic acid the final results would be expressed by,

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

In the case of ferrous sulphate, $FeSO_4$, which corresponds with the oxide FeO, the oxidation product is ferric sulphate, $Fe_2(SO_4)_3$, which corresponds with the oxide Fe_2O_3, and the conversion of $2FeO$ into Fe_2O_3, or that of $2FeSO_4$ (in presence of sulphuric acid) into $Fe_2(SO_4)_3$, requires 1 atom of oxygen,

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Hence 2 molecules of permanganate oxidise 10 molecules of the ferrous salt,

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3.$$

A fixed weight of potassium permanganate oxidises a fixed weight of each of the above substances. If, therefore, a solution of permanganate of *known* concentration is slowly dropped from a burette (p. 256) into a solution containing an unknown weight of the reducing agent (previously mixed with excess of *dilute* sulphuric acid) the colour of the permanganate rapidly disappears at first, but ultimately a point is reached at which the addition of one more drop of permanganate imparts a permanent pink colour to the whole solution. When this stage is reached, the permanganate and the reducing agent have been used in (equivalent) proportions represented by the above and similar equations, so that, if the volume (and concentration) of the permanganate solution which has been added is known, the quantity of the reducing agent originally present may be calculated.

In using potassium permanganate for such *titrations* no indicator (p. 257) is required, but *dilute* sulphuric acid must be added in such quantities to the reducing substance that the solution remains strongly acid in reaction during titration; that is to say, enough sulphuric acid must be present to convert into sulphate the oxide of manganese which is formed by the decomposition of the permanganate.

As the process for which the permanganate is used depends on its oxidising action, the quantity of *available oxygen* contained in 1 litre of the solution is the sole measure of the value of the solution. A standard solution (p. 257), therefore, is generally made of such a concentration that 1 litre contains $\frac{1}{10}$th of a *gram-equivalent* of oxygen. Now $2KMnO_4$ give 5O; hence 316 g. (158 × 2 g.) give 80 g., and 3·16 g. give 0·8 g. of oxygen, or $\frac{1}{10}$th of a gram equivalent of oxygen. A solution which contains 3·16 g. of permanganate in 1 litre may therefore be termed a deci-normal solution (p. 258) when it is used for oxidising purposes.

The halogen acids and their salts must not be present in solutions which are to be titrated with permanganate, as the free acids are oxidised.

Potassium permanganate is not acted on by sodium or potassium hydroxide in aqueous solution, but in presence of reducing agents as well, the permanganate is converted into the manganate, the solution turning green,*

$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O;$$

with excess of the reducing agent, the manganate is then decomposed, giving a precipitate of hydrated manganese dioxide,

$$2K_2MnO_4 + 4H_2O = 4KOH + 2MnO_2, H_2O + 2O.$$

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* Commercial hydroxides of sodium and potassium contain impurities which reduce permanganate to manganate, and therefore these hydroxides seem to bring about this change in absence of a reducing agent.

Hence in *alkaline* solution the final result of the reduction of the permanganate is

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO_2, H_2O + 3O,$$

and 2 molecules of permanganate give 3 atoms of available oxygen. This is the reason why the solution must be kept acid in reaction in doing titrations with permanganate; if the solution were to become alkaline, the oxidising value of the permanganate would be changed.

A solution of sodium permanganate (Condy's fluid) is used as a disinfectant. Sodium permanganate is much cheaper than the potassium salt, but for laboratory purposes it is little used, as it does not crystallise very well and is not easily purified.

THE RELATION OF MANGANESE TO THE HALOGENS.

Although manganese is classed with the halogens, in accordance with the periodic system (p. 720), there is obviously a very great difference between this metal, on the one hand, and the active non-metallic halogens, on the other; the difference, in fact, is so considerable that only a few points of resemblance can be made out. This dissimilarity, when further studied, is seen to be a consequence of the position of manganese in the system, rather than an anomaly which is difficult of explanation. For the properties of every element are, roughly, the mean of those of the elements which immediately precede and follow it in the order of their atomic weights. Now manganese comes between chromium and iron, and thus occupies a position very different from that of any of the halogens; it would be very extraordinary, therefore, if an element so placed showed a close relationship to the sub-family of the halogens.

The resemblance between manganese and the halogens is, in fact, restricted to those compounds which are derived from the typical highest salt forming oxides (p. 722) of this family. Permanganic acid, $HMnO_4$, and perchloric acid,

$HClO_4$ (p. 438), derived respectively from Mn_2O_7 and Cl_2O_7, are both monobasic acids, and are doubtless similar in structure; they are both powerful oxidising agents, and their corresponding salts, as a rule, are isomorphous (p. 324). This likeness, though not very pronounced, affords an instance of the interesting fact that the properties of a compound are determined rather by the structure of its molecule than by the elements of which it is composed. It must be pointed out, however, that in this particular case the conclusion that the molecules are similar in structure is to a great extent based on their similarity in type and in properties, and that there is little direct experimental evidence in support of the structural formulæ assigned to the manganates and permanganates.

The *anhydride*, Mn_2O_7, referred to above is obtained as a very unstable (explosive) oil when potassium permanganate is very cautiously treated with concentrated sulphuric acid (compare footnote, p. 451).

CHAPTER XLVIII.

The Oxygen Family.

Oxygen is the first member of a family of elements which are related to one another in chemical behaviour in much the same kind of way, although perhaps not so closely, as the members of the halogen family; the other elements of this family are sulphur, selenium, and tellurium, and the more distantly related metal chromium.

Oxygen and sulphur, and some of their compounds, have already been described, but a further account of these important elements must be given. Selenium and tellurium are comparatively rarely met with, either in the free or the combined state, and need not be studied in a second year's course. Chromium, on the other hand, gives rise to several important compounds which are frequently used both in the laboratory and on the large scale.

OXYGEN, O_2; AT. WT. 16.

Oxygen (p. 79) may be obtained from many compounds. Certain metallic oxides, as, for example, those of mercury, silver, gold (p. 665), and platinum (p. 712), and certain non-metallic oxides, such as those of chlorine, are decomposed into their elements when they are heated. This, however, is not the general behaviour of oxides, many of which are stable even at the highest temperatures attainable.

In some cases where a metal forms two or more oxides, a higher oxide is converted into a lower oxide when it is strongly heated. Thus oxygen may be obtained by heating lead dioxide (p. 178), red lead (p. 603), manganese dioxide (p. 446), or barium dioxide (p. 458). Oxides which show this behaviour also yield oxygen when they are heated with concentrated sulphuric acid, and do not as a rule give rise to corresponding salts.

Many anhydrides, such as sulphuric anhydride (SO_3), nitric anhydride (N_2O_5), and chromic anhydride (CrO_3), are also decomposed when they are heated, giving a lower oxide. All the oxides of nitrogen are decomposed at the temperature of the electric arc.

The more convenient methods for the preparation of oxygen in the laboratory are (1) by heating potassium chlorate in presence of manganese dioxide (p. 83), and (2) by heating bleaching powder solution in presence of cobalt oxide, which acts as a catalytic agent.

In the latter method bleaching powder (p. 639) is made into a thin paste with water, a few drops of a solution of a cobalt salt are added, and the mixture is gradually heated in a flask which is provided with a delivery-tube. Oxygen is soon evolved, and may be collected in one of the usual ways.

The cobalt salt is decomposed by the bleaching powder solution, which acts as if it contained calcium hydroxide and calcium chlorohypochlorite (p. 640), and a black precipitate of cobaltic hydroxide is formed,

$$2Co(NO_3)_2 + 2Ca(OH)_2 + CaCl(OCl) + H_2O = 2Co(OH)_3 + CaCl_2 + 2Ca(NO_3)_2 ;$$

this substance acts as a catalytic agent, and hastens the decomposition of the calcium chlorohypochlorite,

$$2CaCl(OCl) = 2CaCl_2 + O_2.$$

The preparation of oxygen on the commercial scale is accomplished in various ways. **Brin's process** is based on the reversible reaction expressed by the equation,

$$2BaO + O_2 \longleftrightarrow 2BaO_2.$$

Barium monoxide (p. 646) is heated in iron retorts, and air, carefully purified from moisture and carbon dioxide, is pumped into the retorts, whereby the pressure, and therefore the *concentration* (p. 355), of the atmospheric oxygen is increased. The oxygen is then absorbed, with formation of barium dioxide, and the nitrogen escapes through suitable valves. As soon as the monoxide has been thus transformed into the dioxide, the gas in the retorts is pumped out, whereupon the barium dioxide begins to decompose into barium monoxide and oxygen, because the *concentration* of the oxygen is diminished. The liberated oxygen is removed as fast as it is formed, and is pumped into iron cylinders; by thus keeping down the pressure (concentration) of the oxygen, the decomposition continues ($2BaO_2 \longrightarrow 2BaO + O_2$) until most of the dioxide is changed, although the temperature is the same as that at which the reverse action occurred under the greater pressure (concentration). The gas so obtained contains about 98 per cent. of oxygen.

Another method of obtaining oxygen from the air is described later (p. 602).

The *oxides* (p. 85) are substances of such importance that a few general statements regarding their methods of formation, properties, and classification may be given here even at the risk of repetition.

Most elements form one or more oxides; the more notable exceptions are fluorine, bromine, and the members of the argon family (p. 681). Nearly all those elements which form oxides do so when they are heated in oxygen (the more important exceptions being silver, gold, and platinum), but the usual methods of preparing *metallic* oxides are (1) by heating hydroxides (p. 250), (2) by heating nitrates (p. 242), and (3) by heating carbonates (p. 276).

Many oxides undergo double decomposition with acids, giving the corresponding salt (p. 284) and water. Such oxides are called basic oxides (p. 254), and an element which forms at least *one* basic oxide is classed as a metal (p. 255). Some oxides unite directly with water, forming hydroxides (p. 250), this behaviour is shown by most anhydrides, but by only a relatively small number of the basic oxides, namely, principally by those of the alkali metals (p. 666) and the metals of the alkali earths (p. 637). An anhydride is an oxide which combines with water to form an acid, and any element which gives anhydrides or acid-forming oxides *only* is classed as a non-metal.

When a metal forms several oxides one or more of the higher oxides may be anhydrides, as, for example, in the case of manganese (p. 451) and of chromium (p. 505).

Some oxides cannot be classed either as basic oxides or as anhydrides. Barium dioxide, BaO_2, for example, does not give rise to corresponding salts; it reacts with acids giving salts which are derived from barium monoxide, BaO. Such oxides are classed as *basic peroxides*. A few oxides, such as Mn_3O_4, Pb_3O_4, do not fall into any of the classes already mentioned, and may be regarded as salts (compare pp. 447, 603). Nitric oxide, NO, and a few other oxides do not correspond with any of these classes.

The Valency of Oxygen.—In nearly all its compounds oxygen seems to be bivalent; there are, however, a few compounds the behaviour of which is best explained on the assumption that they contain quadrivalent oxygen.*

The Unit of Atomic Weight.—Although in beginning the study of chemistry it is more convenient to express the relative weights of the atoms of the different elements in terms of that of an atom of hydrogen, which is taken as unity, it makes, of course, no difference to the *relative* values of the atomic weights what particular standard is chosen. Now when the weight of an atom of hydrogen is taken as unity, the atomic weight of oxygen is 15·88; if, however, the atomic weight of oxygen is put = 16, although that of hydrogen then becomes 1·008, the atomic weights of many of the elements approximate more closely to whole numbers than when that of hydrogen is taken = 1.

Thus when O = 16 some of the values are,

H	O	C	N	Na	S	Cl	Ca	Ag
1·008	16	12·00	14·01	23·00	32·07	35·46	40·09	107·88;

but when H = 1 the values are,

H	O	C	N	Na	S	Cl	Ca	Ag
1	15·88	11·9	13·9	22·88	31·82	35·18	39·7	107·1.

There is another reason why it is perhaps better to take O = 16 as the standard, namely, that the equivalents, and therefore the atomic weights (p. 198), of many elements are determined from analyses of their oxides; that is to say, the atomic weights are based directly on the oxygen standard. In order to express the atomic weights thus determined on the basis of H = 1, it is necessary to know the ratio H : O. This ratio, according to the most trustworthy determinations, is 1 : 15·88; but if further more accurate determinations were to give a different ratio, it would then be necessary to recalculate and alter the atomic weights of the other elements.

In the table (p. 201) the atomic weights are given on the basis H = 1, but in the table given later **(on last page)** the standard is O = 16, and all the atomic weights in this volume (Part II.) refer to this standard.

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* Compare hydrogen peroxide (p. 475). The best-known compounds in which oxygen seems to be quadrivalent are certain carbon compounds which cannot be described here.

When all the atomic weights are thus increased, the volume at N.T.P. occupied by the **gram-molecule** of a gas is, of course, also greater than before, and instead of 22·25 litres (p. 197) it is $22{\cdot}25 \times \frac{2{\cdot}016}{2} = 22{\cdot}4$ litres.

Ozone, O_3.

It has long been known that some substance having a very penetrating and characteristic smell is produced when electric sparks pass through air; but the matter was first carefully investigated in 1840 by Schönbein, who named this substance **ozone** and studied many of its properties. It was proved later by Andrews and Tait that ozone consists of the element oxygen.

A simple way of preparing ozone is to pass the *silent discharge* (p. 300) through pure dry oxygen, and many forms of apparatus have been devised suitable for this purpose. One of the more recent ones is shown in fig. 100 (p. 463).

This apparatus is made entirely of glass. It consists of the tube (*a*, *a*), which is closed below, and which contains sulphuric acid; this tube is concentrically placed in the wider tube (*b*), into which it is sealed at the top. The outer cylindrical jacket (*c*) also contains sulphuric acid. Pure dry oxygen is passed into the tube (*b*) through the tap (*d*), and its escape through the U-tube being prevented by the sulphuric acid seal, it passes upwards, as indicated by the arrows, between the two concentric glass surfaces, which are in contact with the sulphuric acid. The platinum terminals (*e*, *e*) pass through the rubber stopper and the glass jacket (*c*), respectively, into the sulphuric acid, and are connected with the terminals of a Rhumkorff's coil; the silent discharge may thus be passed through the oxygen which is flowing between the two concentric glass surfaces.

In a few moments after the discharge has been started the characteristic odour of ozone is noticeable, and it can be shown that the oxygen escaping from the outlet (*f*) contains some substance which is much more active than oxygen.

Thus when a piece of paper which has been dipped in starch paste containing a little potassium iodide is held near the outlet tube the paper immediately becomes blue; ozone liberates iodine from potassium iodide,* and *free* iodine gives a blue colour with starch (p. 415). When a paper coated with a thin layer of (black) lead sulphide, PbS, is held near the outlet-tube the paper becomes white, because the lead sulphide is oxidised to lead sulphate, $PbSO_4$. When the gas is passed through a dilute solution of 'indigo'† the blue colour gradually disappears, because the 'indigo' is oxidised to some colourless substance. Oxygen does not give any of these reactions. The tests so far described are not characteristic of ozone, as there are certain other substances which behave like ozone under the above conditions so far as the *observed* results are concerned.

One property of ozone, however, serves to distinguish it from all other substances; it produces a black film on a clean bright surface of silver, owing to the formation of silver peroxide. Unfortunately the test is not a very delicate one.

In order to show this reaction a piece of silver foil is very carefully cleaned by rubbing it with well-washed sand, and is then heated in a Bunsen-flame for a few moments;

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* The reaction which occurs here is a very complex one, but one result may be expressed by the equation,

$$2KI + O_3 + H_2O = 2KOH + I_2 + O_2.$$

Although iodine is acted on by potassium hydroxide, giving potassium iodide and hypoiodite (p. 430), iodine is liberated from a neutral solution of potassium iodide by ozone, possibly owing to the oxidation of the potassium hydroxide to a peroxide.

† Prepared by dissolving indigo in concentrated sulphuric acid and then diluting with water.

while still hot, the foil is held close to the outlet of the ozoniser.

Silver perfectly free from silver oxide does not show this reaction. Silver does not oxidise to any appreciable extent when it is heated in the air or in oxygen, and silver oxide is readily decomposed when it is heated alone; nevertheless it seems that a minute trace of silver oxide is formed when the metal is heated in the air, and that this minute trace is required for the ozone reaction.

Another characteristic test for ozone is its behaviour towards mercury. When very carefully purified mercury is exposed to ozonised oxygen, say, in a test-tube, it loses its mobility to some extent and adheres to the glass surface, owing doubtless to the formation of an extremely thin film of oxide.

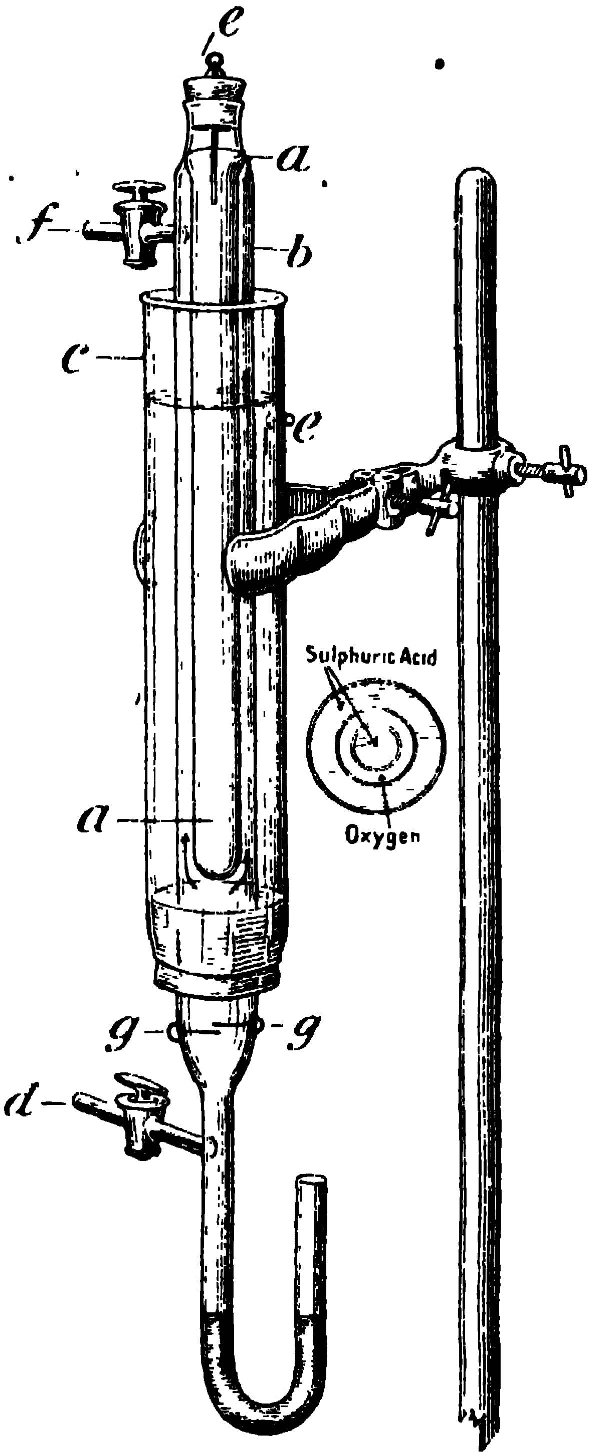

Fig. 100.

The stream of ozonised oxygen issuing from the ozoniser immediately ceases to give all the above reactions when a small glass tube is attached to the outlet tube (*f*) * and the gas passing through this tube is gently heated with a Bunsen-burner. Ozone is rapidly and completely converted into oxygen at temperatures above about 250°.†

Ozone is also decomposed by vegetable matter, such as cork and india-rubber (which it oxidises), so that these materials must not be used in any part of an ozoniser which is exposed to the gas. Ozone is completely absorbed by oil of turpentine (p. 125) and by many other carbon compounds.

When ozonised oxygen is led through a glass tube which is cooled to – 181° the ozone condenses to a very deep-blue liquid of boiling-point – 119°, and only a little oxygen liquefies with it; the pure ozone, which may be obtained by the fractional distillation or evaporation (p. 32) of this liquid, is to a great extent converted into oxygen when it reaches the ordinary temperature of a room.

Since ozone is produced from oxygen, and is converted into oxygen when it is heated, it must consist entirely of oxygen matter. Now these two gases cannot differ from one another, as may two solids, in the arrangement of their molecules (compare p. 214), so the difference between them must be due to some difference in the nature of their *molecules.* Therefore, since oxygen molecules consist of two atoms (p. 199), those of ozone might consist of one, three, four, or more. In order to establish the relation between oxygen and ozone it is necessary to find the molecular weight of ozone from its density; but as pure ozone is not stable at ordinary temperatures, the experiments must be made with ozonised oxygen in which the proportion of ozone is determined afterwards by absorption with turpentine.

For this purpose a large glass globe full of oxygen is carefully weighed; it is then filled with ozonised oxygen under the same conditions of temperature and pressure and weighed again. After this second weighing the globe is cooled and the tap is opened under turpentine, some of which is then drawn into the globe. After the tap has been closed, and the turpentine shaken with the gas for some time, the tap is again opened under turpentine and the globe is left to regain its original temperature. The total volume of the turpentine which is then contained in the globe is measured, and this volume is equal to that of the ozone which has been absorbed. From these data the weight of this volume of ozone may be calculated, and the density of the gas is thus found to be 24.

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* The connection is made by means of a pierced cork which has been coated with paraffin wax.

† Ozone is also decomposed when it is 'sparked' (p. 298), and the platinum terminals (*a*, *g*, fig. 100) may be used to show this decomposition. The taps of the tubes (*d*) and (*f*) being closed, an increase in volume is observed on 'sparking.'

Example.—Weight of globe full of oxygen, 52·8540 g. Weight of globe full of ozonised oxygen, 52·9125 g. Volume of ozone (corrected to N.T.P.), 80 c.c. Hence 80 c.c. of ozone weigh $52{\cdot}9125 - 52{\cdot}8540 = 0{\cdot}0585$ g. *plus* the weight of 80 c.c. of oxygen (which is $1{\cdot}43 \times \frac{80}{1000} = 0{\cdot}1144$ g.). Since 80 c.c. of ozone weigh 0·1729 g., 1000 c.c. weigh 2·16 g., and the density, therefore, is $\frac{2{\cdot}16}{0{\cdot}09} = 24$.

The density of ozone may also be determined indirectly, but not accurately, in the following manner: A small, sealed, thin-walled tube containing turpentine is suspended in the ozoniser (fig. 100, p. 463) in such a way that it can be broken by rotating the inner tube (*a*).* The ozoniser is then filled with dry oxygen at atmospheric temperature and pressure, and the taps (*d* and *f*) are closed. The discharge is then passed for some time, the apparatus is allowed to cool, and the contraction of the gas is measured by noting the movement of the sulphuric acid in the U-tube. Let this contraction be x c.c.

The bulb containing the turpentine is then broken, and after the absorption of the ozone is complete the contraction due to this absorption is measured. This is found to be $2x$ c.c. Therefore the volume of oxygen which has disappeared is $3x$ c.c., and this volume of oxygen gave $2x$ c.c. of ozone. As three volumes of oxygen of density 16 give two volumes of ozone, the density of ozone is 24.

The density of ozone being 24, its molecular weight is 48;

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* In ozonisers used for this purpose the tube (*a*, *a*) is ground, and not sealed, into the outer tube (*b*).

the molecule of ozone, therefore, consists of 3 atoms of oxygen, and is represented by O_3. This conclusion is confirmed by measurements of the rate of diffusion (p. 168) of ozone contained in ozonised oxygen.

The relation between the two gases, therefore, is expressed by the equation,

$$\underset{\text{3 vols.}}{3O_2} \longleftrightarrow \underset{\text{2 vols.}}{2O_3}$$

The change from left to right is an endothermic reaction, and the energy required to bring it about is supplied in the ozoniser in the form of electrical energy.*

Since ozone differs from oxygen in chemical properties and yet is made of the same form of matter, it is sometimes termed an allotropic form of oxygen (pp. 215, 479); it is also referred to as 'active oxygen.'

Ozone shows three distinct types of reactions. (1) It combines directly with, and therefore is absorbed by, many carbon compounds, such as turpentine and other unsaturated substances. (2) It oxidises many substances and at the same time gives free oxygen, as, for example, in the case of lead sulphide,

$$PbS + 4O_3 = PbSO_4 + 4O_2.$$

(3) It decomposes in presence of many substances, such as platinum black (p. 712), lead dioxide, and manganese dioxide, and is completely converted into oxygen, the substances in question acting as catalytic agents.

Ozone is produced, together with hydrogen peroxide, in many reactions in which moist gaseous oxygen takes part (p. 477).

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* In the ozoniser described above the conditions are such that equilibrium is established when the percentage of ozone in the product (*ozonised oxygen*) is not more than about 3 to 8 per cent. Ozonised oxygen containing as much as 23 per cent. by weight of ozone can be obtained by the electrolysis of diluted sulphuric acid of specific gravity less than 1·22, using electrodes of which only an extremely small surface is exposed to the solution.

WATER, H_2O.

The synthesis of water by Cavendish (p. 105), its decomposition by Lavoisier (p. 106), its quantitative analysis by weight (p. 110), and its quantitative analysis by volume (p. 188) have already been described.

More recently the composition of water by weight has been very carefully determined by Morley, by burning weighed quantities of pure hydrogen in weighed quantities of pure oxygen and weighing the water thus formed. His results gave the ratio, $H : O = 2 : 15{\cdot}88$ by weight and $2{\cdot}0027 : 1$ by volume.

The high boiling-point of water compared with that of hydrogen sulphide, and many other properties of water which are of an apparently abnormal kind, are accounted for by the fact that the molecules of (liquid) water are associated to form complexes $(H_2O)_n$, where $n = 2$ or 3.

When any ordinary sample of water is distilled, the distillate contains traces of dissolved gases, such as carbon dioxide, ammonia, and oxygen, because, although these gases are expelled when the water is boiled, they dissolve again in the condensed steam. Further, when distilled water comes into contact with ordinary glass apparatus, it has an appreciable solvent action on the silicates contained in the glass (p. 293), and becomes contaminated with traces of alkali hydroxides and salts. The impurities which are thus taken up may be present in such minute quantities that it is almost impossible to detect them by chemical examination, but even when this is the case their presence increases in a very marked manner the electrical conductivity of the sample.

Pure water, practically speaking, is a non-conductor; the presence of impurity and some idea of its quantity is therefore most easily ascertained by measuring the conductivity of the sample.

In order to obtain water of a very high degree of purity, it is distilled in a vessel made of copper or of tin-plate (p. 588), using condensers of tin and a receiver of the same metal or of best Jena glass. The first portions of the water are neglected, and the apparatus is so constructed that the pure distilled water ('conductivity water') is cut off from direct communication with the atmosphere—a matter of great importance.

It has already been noted that many oxides combine directly with water, forming hydroxides. In the case of those metallic oxides which do not unite with water directly, the corresponding hydroxides may generally be obtained by treating a salt of the metal with sodium hydroxide in aqueous solution,

$$\mathrm{MnCl_2 + 2NaOH = Mn(OH)_2 + 2NaCl}$$
$$\mathrm{CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4}.$$

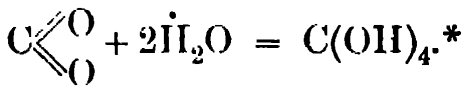
Some hydroxides (e.g. silver hydroxide) are so unstable that when prepared by this method they immediately decompose, giving water and the oxide, so that, although they may in some cases exist in aqueous solution, they cannot be isolated.

Theoretically, however, for every oxide there may exist a corresponding hydroxide, which can be formed by the direct union of the molecules of the oxide with those of the water. This union is rendered possible by a rearrangement of the atoms of both the molecules. Every atom of oxygen in the oxide is assumed to be combined to the other element by *both* its hooks or bonds (p. 331); but this arrangement may be altered in such a way that the two elements remain united by only *one* hook or bond of each, leaving free for other combinations one hook of the oxygen atom and one of the other element. When, therefore, an oxide unites with water, the grouping $\mathrm{X=O}$ becomes transiently $\mathrm{X}<^{\mathrm{O}}$, and the latter combines with a hydrogen atom and a hydroxyl-group from the water molecule to form the hydroxide $\mathrm{X}<^{\mathrm{O-H}}_{\mathrm{O-H}}$.

In this way there are formed twice as many hydroxyl-groups as there are atoms of oxygen in the original oxide.

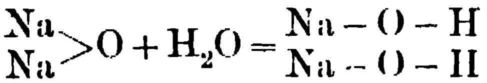
Now when the oxide is that of an element of even valency, one molecule of the hydroxide is formed from every molecule of the oxide, as, for example,

$Ca{:}O + H_2O = Ca(OH)_2$

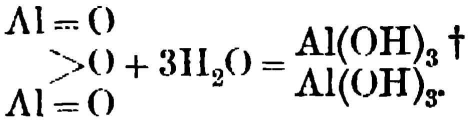


$$C\!\!\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + 2H_2O = C(OH)_4.$$*

When, however, the oxide is that of an element of odd valency, it contains two atoms of the element linked together by oxygen, and in the combination with the water molecules the 'link' is broken, *two* molecules of the hydroxide being formed from *one* of the oxide,



$$\begin{matrix}Na\\ Na\end{matrix}\!\!>O + H_2O = \begin{matrix}Na-O-H\\ Na-O-H\end{matrix}$$



$$\begin{matrix}Al=O\\ \quad>O\\ Al=O\end{matrix} + 3H_2O = \begin{matrix}Al(OH)_3\\ Al(OH)_3.\end{matrix}$$†

These examples will illustrate the relation between an oxide and the *corresponding* hydroxide; the valency of the element is the same in both compounds and corresponds with the number of the univalent hydroxyl-groups.

As the different elements vary in valency from 1 to 8, the following types of hydroxides are *theoretically* possible,

$$X(OH),\quad X(OH)_2,\quad X(OH)_3,\quad X(OH)_4,\quad X(OH)_5,$$
$$X(OH)_6,\quad X(OH)_7,\quad X(OH)_8.$$

Further, since many elements show a variable valency, a given element may form two or more of the above types of hydroxides. Manganese, for example, may give the compounds,

$$Mn(OH)_2,\quad Mn(OH)_4,\quad Mn(OH)_6,\quad Mn(OH)_7.$$

The various hydroxides which are thus theoretically derived from the known oxides of an element are not always actually obtainable. When the number of hydroxyl-groups in a molecule exceeds *three* the theoretically possible hydroxide is often unstable, but in its place there may exist a compound formed from it by loss of the elements of water. Thus the hydroxide $C(OH)_4$ does not exist, except possibly in aqueous solution, but carbonic acid is derived from it,

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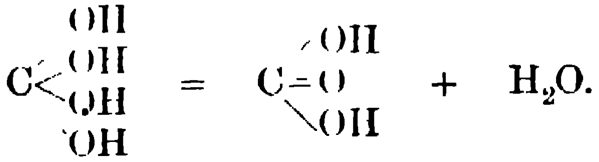
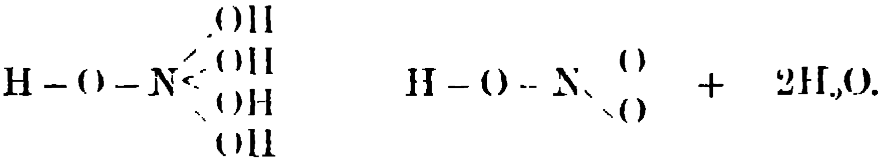
* The compound represented by this formula is not actually obtainable.

† Aluminium oxide does not unite *directly* with water.



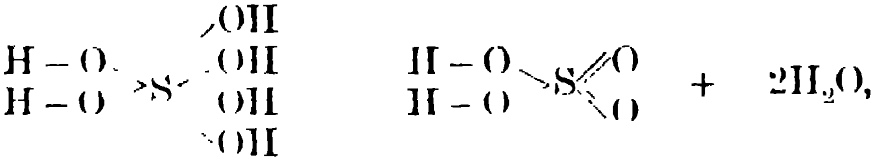
$$C(OH)_4 = C{=}O(OH)_2 + H_2O.$$

The hydroxide $N(OH)_5$ does not exist, except possibly in aqueous solution, but nitric acid is derived from it,



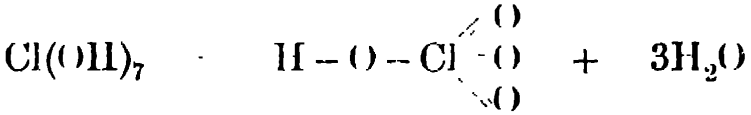
$$H-O-N(OH)_4 \quad H-O-N(O)(O) + 2H_2O.$$

Similarly, the hydroxide $S(OH)_6$ gives rise to sulphuric acid,

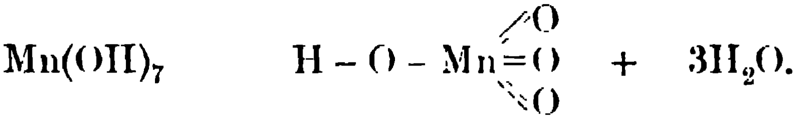


$$(H-O)_2{>}S(OH)_4 \quad (H-O)_2{>}S(O)(O) + 2H_2O,$$

and the hydroxides $Cl(OH)_7$ and $Mn(OH)_7$ give rise to perchloric and permanganic acids respectively,



$$Cl(OH)_7 = H-O-Cl(O)(O)(O) + 3H_2O$$



$$Mn(OH)_7 \quad H-O-Mn(O)(O)(O) + 3H_2O.$$

All the oxygen-containing acids are compounds of this type, and their displaceable hydrogen is directly combined with oxygen. The *normal* acid hydroxides, that is to say, those compounds in which *all* the oxygen atoms are united to hydrogen, are often called *ortho*-acids, while those compounds derived from ortho-acids by the loss of the elements of water are often called *meta*-acids. Thus the hydroxides $C(OH)_4$ and $Si(OH)_4$ are known as ortho carbonic and ortho-silicic acid respectively, while the compounds $CO(OH)_2$ and

$SiO(OH)_2$ are called meta-carbonic and meta-silicic acid respectively. Unfortunately these terms are not used in a very systematic manner; the compound $PO(OH)_3$, for example, is called ortho-phosphoric acid, whereas this name should be given to the unknown hydroxide, $P(OH)_5$, from which ortho-phosphoric acid is derived.

HYDROGEN PEROXIDE, H_2O_2.

Hydrogen peroxide (or hydrogen dioxide) was first obtained by Thénard (1818), who prepared it in aqueous solution by treating barium peroxide (dioxide) with *dilute* acids,

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

By using an acid which forms an *insoluble* barium salt and employing the right proportions of barium peroxide and acid, there results a solution which, when it is filtered, contains only hydrogen peroxide (footnote, p. 433). Hence an aqueous solution of hydrogen peroxide is conveniently prepared by slowly adding barium peroxide to *cold*, dilute sulphuric acid until the solution is just neutral, or by passing carbon dioxide through water containing barium peroxide in suspension,

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$
$$BaO_2 + H_2CO_3 = BaCO_3 + H_2O_2.$$

The solution is then filtered and evaporated at ordinary temperatures in a vacuum, whereupon hydrogen peroxide remains as a colourless, syrupy liquid.

Ordinary commercial barium dioxide is only slowly acted on by dilute acids and gives poor results because the impurities which it contains decompose the hydrogen peroxide on the solution being evaporated. As the purification of the barium dioxide is a troublesome task, concentrated aqueous solutions of hydrogen peroxide are best prepared by gradually adding sodium peroxide (p. 671) to *excess* of well-cooled dilute sulphuric acid,

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

Although hydrogen peroxide is decomposed in aqueous solution by many salts, sodium sulphate does not cause its decomposition, and a pure aqueous solution of the peroxide may be obtained from the impure solution by distillation under reduced pressure.* From this product the pure peroxide may be isolated by further fractional distillation under reduced pressure.

Hydrogen peroxide has a neutral or faintly acid reaction and a bitter taste, and is poisonous; its sp. gr. is about 1·5, its melting-point – 2°, and it boils at 84–85° under a pressure of 68 mm. The *pure* compound does not change spontaneously, but in presence of even traces of many other substances it may explode violently, and this is true also in the case of its concentrated aqueous solutions.

Even dilute solutions of hydrogen peroxide decompose when they contain free alkalis or certain salts. For this reason commercial solutions generally contain a little sulphuric acid, which prevents them from becoming alkaline when they are kept in glass bottles,† and thus increases their stability.

Aqueous solutions of hydrogen peroxide are also decomposed and oxygen is evolved when they are treated with finely divided silver, platinum, and many other metals, or with many oxides, such as manganese dioxide, or litharge; in this decomposition, which is strongly *exothermic*, water and oxygen are formed,

$$H_2O_2 + H_2O_2 = 2H_2O + O_2,$$

and the added metal or other substance is not permanently changed, but acts as a catalytic agent.

The fact that hydrogen peroxide, when decomposed, gives water and oxygen *only* renders it possible to determine its composition by weight in a relatively simple manner (p. 474).

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* The object of reducing the pressure is to lower the boiling-point, and thus avoid the decomposition of the peroxide.

† Water kept in a glass bottle soon becomes alkaline, owing to its solvent action on the components of the glass (p. 293). Hydrogen peroxide is often stored in bottles which are coated on the inside with paraffin wax.

Hydrogen peroxide is an active oxidising agent towards many substances. It liberates iodine from potassium iodide in presence of *acids*,*

$$2HI + H_2O_2 = 2H_2O + I_2,$$

and immediately imparts a blue colour to starch-potassium-iodide paper; it oxidises lead sulphide to lead sulphate, sulphur*ous* to sulphur*ic* acid, and hydrogen sulphide to sulphur and water,

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$
$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$$
$$SH_2 + H_2O_2 = S + 2H_2O.$$

It also oxidises and bleaches indigo and litmus, and many other substances (p. 475).

Hydrogen peroxide also acts as a reducing agent towards a few substances. Thus it reduces the oxides of silver and of mercury to the metals,

$$Ag_2O + H_2O_2 = 2Ag + O_2 + H_2O$$
$$HgO + H_2O_2 = Hg + O_2 + H_2O;$$

and it reduces lead dioxide to lead monoxide,

$$PbO_2 + H_2O_2 = PbO + O_2 + H_2O.$$

It also reduces potassium permanganate: in alkaline solution to hydrated manganese dioxide (p. 446); in acid solution to a manganous salt,

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

In these, and in all cases in which hydrogen peroxide acts

*** Oxygen is also evolved in this interaction. When a *neutral* solution of hydrogen peroxide is added to a neutral solution of potassium iodide oxygen is evolved, but there is no appreciable liberation of iodine; nevertheless a starch-potassium-iodide paper moistened with the solution of the peroxide immediately becomes blue.**

as a reducing agent, one molecule of oxygen is evolved for every molecule of hydrogen peroxide which takes part in the reaction. It seems, therefore, that an atom of oxygen from the hydrogen peroxide combines with an atom of oxygen from the other substance to form a molecule of oxygen, and in this way two substances which generally behave as oxidising agents are both reduced.

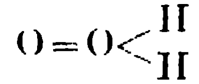
All the reactions described above may be used in testing for hydrogen peroxide, but they are not *characteristic* reactions; that is to say, other substances (such as ozone) give similar outward results. A very characteristic, and also a very delicate, test for hydrogen peroxide is the following. The solution to be tested is acidified with a little dilute sulphuric acid, and placed in a bottle together with some ether; a drop of a solution of potassium dichromate is then added, and the bottle is closed with a glass stopper and vigorously shaken for a moment. The ether which then rises to the surface of the aqueous solution is coloured a deep blue if hydrogen peroxide was present, owing to the formation of a very unstable substance (probably perchromic acid, $HCrO_5$), which rapidly decomposes.

The *composition* of pure hydrogen peroxide may be determined by dissolving a weighed quantity of the substance in a little water, and then passing the solution into a eudiometer-tube which is filled with mercury; on being gently heated the peroxide is completely decomposed, and the weight of the liberated oxygen is calculated from the corrected volume of the gas.

Example.—0·1 g. of hydrogen peroxide gave 32·8 c.c. of oxygen at N.T.P. Since 32·8 c.c. of oxygen weigh 0·00143 × 32·8 = 0·0469 g., the hydrogen peroxide has given 46·9 per cent. of oxygen. Knowing that the only other product is *water* (53·1 per cent. by difference), the ratio $O : H_2O$ is deduced in the usual way,

$$46{\cdot}9 \div 16 = 2{\cdot}93 \; O$$
$$53{\cdot}1 \div 18 = 2{\cdot}95 \; H_2O.$$

It is thus *found that hydrogen peroxide has the empiric* formula HO. Its molecular weight may be determined by the cryoscopic method, and is found to be 34; the molecular formula, therefore, is H_2O_2.

Although hydrogen peroxide is a relatively simple compound, its *constitution* or *structure* has not yet been established quite satisfactorily; and there is some doubt as to whether the formula $H-O-O-H$ or  $O=O<^{H}_{H}$ should be used to represent the arrangement of the atoms in the molecule. The readiness with which the compound decomposes into water and oxygen seems to point to the second formula (in which one of the oxygen atoms is represented as being quadrivalent), but a study of certain organic derivatives of hydrogen peroxide seems to indicate that the first formula is the better expression.

This question of the constitution of hydrogen peroxide is of some general importance, inasmuch as the constitution of barium peroxide, sodium peroxide, and other peroxides is probably similar to that of this hydrogen compound.

Hydrogen peroxide is used commercially in bleaching delicate materials, such as silk, feathers, hair, and ivory, which are damaged by the application of bleaching powder. It is also used as an antiseptic in surgery, and in renovating oil-paintings. The hydrogen sulphide present in the air of towns acts on the white-lead (p. 600) and other lead compounds which are often used in oil-painting, and changes them into (black) lead sulphide; hydrogen peroxide restores the original appearance, because it oxidises the lead sulphide to colourless lead sulphate (p. 473).

The *quantity* of hydrogen peroxide in an aqueous solution may be ascertained by decomposing a known weight (or volume) of the solution with excess of potassium permanganate in presence of sulphuric acid, and then measuring the volume of the oxygen which is liberated.

It has been proved experimentally that in this reaction one-half of the liberated oxygen comes from the hydrogen peroxide and the other half from the permanganate, in accordance with the equation,

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2;$$

hence 1 gram-molecule (or 22·4 litres at N.T.P., compare p. 461) of oxygen corresponds with 1 gram-molecule of the peroxide.

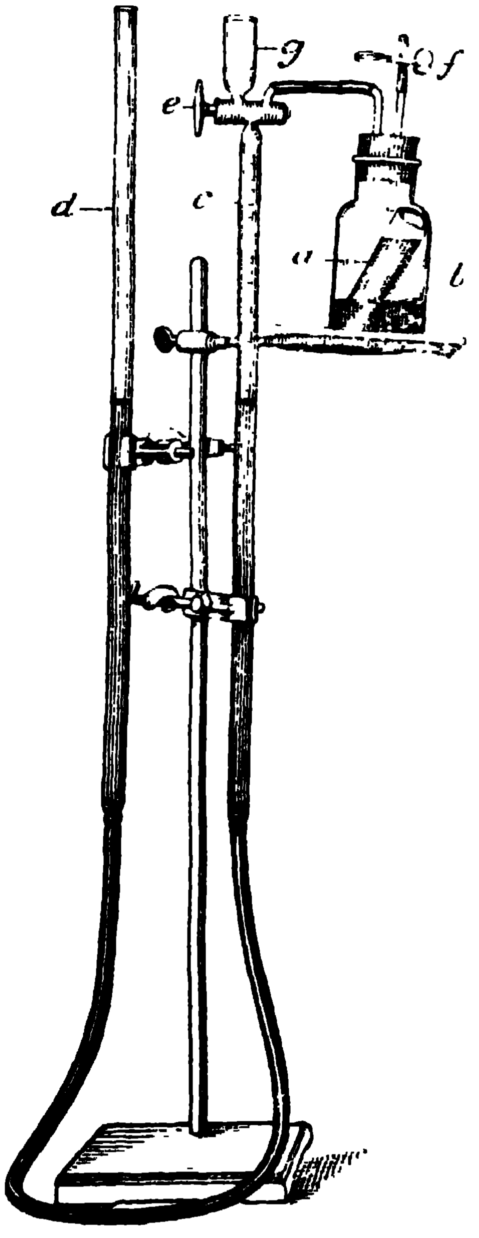


Fig. 101.

The estimation is conveniently carried out as follows: A measured (or weighed) quantity of the solution contained in the small tube (*a*, fig. 101) is placed in the bottle (*b*), which contains an *excess* of potassium permanganate and dilute sulphuric acid. The bottle is connected, as shown, to the *nitrometer* (*c*). By raising the reservoir (*d*) and opening the 3-way tap (*e*) to the air, the graduated tube (*c*) is completely filled with the water (or mercury) contained in the nitrometer. The tap is now turned so that the tube (*c*) is cut off from the air and from the bottle (*b*). The pinch-cock (*f*) is momentarily opened so that the air in the bottle may be brought to barometric pressure, the bottle and the tube (*c*) are connected by turning the 3-way tap, and the reservoir (*d*) is lowered.

The solution of the peroxide is now carefully brought into contact with the acidified permanganate by tilting the bottle (*b*), and when the two liquids have been thoroughly mixed the apparatus is allowed to cool. The reservoir (*d*) is then raised until the water-levels are the same (as shown in the fig.), and the volume of water which has been displaced from the graduated nitrometer-tube (*e*) is observed. As the gas in this tube is under the same pressure (P) and at the same temperature (t) as was the air at the commencement of the experiment, the volume of the liberated oxygen (saturated with aqueous vapour, p. 156) at P and t° is equal to that of the water which has been displaced.

The concentration of a solution of hydrogen peroxide is often expressed in terms of the *volume* of oxygen which is liberated under these conditions; thus a 25-volume solution is one which gives 25 c.c. of oxygen at N.T.P. for every 1 c.c. of solution. As one gram-molecule (34 g.) of hydrogen peroxide gives with permanganate 22·4 litres of oxygen, a 25-volume solution contains $\frac{25}{22,400} \times 34$ g. of peroxide in 1 c.c.

Hydrogen peroxide is formed, probably together with ozone, when moist phosphorus is exposed to air or oxygen; also when turpentine (p. 125),* zinc, lead, and many other substances are exposed to molecular oxygen (O_2) in presence of water. In these cases it is easy to show that some oxidising agent has been produced by testing the gas (air or oxygen) or water with starch-potassium-iodide papers; but it is often difficult to ascertain whether hydrogen peroxide, or ozone, or both, have been formed, because they may be present in very small quantities only. Thus it is very difficult to prove whether ozone, or hydrogen peroxide, or both, are present in the atmosphere.

Hydrogen peroxide and ozone are both formed during the action of molecular hydrogen on molecular oxygen, that is to say, when the one gas burns in the other.

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* The formation of hydrogen peroxide and of ozone during the atmospheric oxidation of turpentine has been denied.

The formation of hydrogen peroxide may be shown by playing the oxyhydrogen flame on the surface of a solution of titanium dioxide in sulphuric acid, when a yellowish colouration is produced. This test is not given by ozone.

The formation of ozone may be shown by playing the point of a hydrogen flame on the surface of a bright piece of silver, prepared as already described (p. 462).

Hydrogen peroxide is produced during the electrolysis of dilute sulphuric acid under certain conditions (footnote, p. 466), and ozone is said to be formed by the action of acids on barium peroxide (compare hydrogen peroxide, p. 471).

Autoxidation.—The formation of ozone during the oxidation of certain substances by atmospheric oxygen was at one time accounted for by supposing that some of the oxygen molecules were resolved into their atoms, and that, while some of these atoms oxidised the given substance, others combined with some of the oxygen molecules to form ozone. To such spontaneous oxidations brought about by free oxygen the term *autoxidation* has been given, but the original explanation of the formation of ozone has been abandoned.

During the oxidation of an autoxidisable substance, the oxidation of other substances which by themselves do not undergo autoxidation may be brought about; this is possibly due to the formation of ozone or hydrogen peroxide, but the phenomena have not yet been satisfactorily explained.

CHAPTER XLIX.

Sulphur and its Compounds.

SULPHUR, S_8; AT. WT. 32.

It used to be supposed that native sulphur (p. 211) had been formed from volcanic gases by the interaction of hydrogen sulphide and sulphur dioxide (p. 289), but it is now considered more probable that the naturally occurring deposits of this element have been produced by the action of bacteria. Certain organisms, the 'sulphur bacteria,' have the property of absorbing sulphur from hydrogen sulphide; as this gas is often formed in considerable quantities by the decomposition of animal or vegetable matter in presence of water which is rich in sulphates, it may serve as 'food' for the sulphur bacteria, and when the dead organisms decompose, the sulphur which they contain is left as a deposit.

Although the different varieties of sulphur (rhombic, monoclinic, plastic, and amorphous, pp. 212–214) are often spoken of as allotropic forms of sulphur, it is not known whether the relationship between them is or is not comparable to that between oxygen and ozone; in the latter case it can be proved that the *molecules* of the two allotropic forms of the element are different, but in the case of sulphur it is not known whether the various varieties consist of identical molecules, or whether some of them have a different molecular complexity from others. As, however, the rhombic and monoclinic forms of sulphur are so easily changed one into the other, and are so very similar in chemical properties, it seems probable that their molecules are identical, but that these molecules are differently arranged in the two crystalline varieties. The term 'allotropic form' is thus often used without any reference to the nature of the relationship between the distinguishable varieties of an element.

The *valency* of sulphur is variable. In hydrogen sulphide sulphur is bivalent, but in its oxides and hydroxides it is either quadrivalent or sexvalent, as indicated in the structural formulæ of these compounds which are given later.

Sulphur unites with chlorine at ordinary temperatures, giving first *sulphur monochloride*, S_2Cl_2, then the *dichloride*, SCl_2, and finally (in the cold) the *tetrachloride*, SCl_4. The monochloride is a yellow liquid (b.p. 138°), and is used in vulcanising india-rubber; it is decomposed by water,

$$2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S.$$

HYDROGEN SULPHIDE, H_2S.

The combination of hydrogen and sulphur to form hydrogen sulphide (p. 216) is a reversible reaction, as hydrogen sulphide dissociates below a red heat (p. 217). The compound is formed in small proportions when hydrogen is passed through boiling sulphur, as may be easily shown by exposing a lead-acetate paper * to the escaping gas after the gas has been cooled and filtered through cotton-wool in order to free it from particles of sulphur.

In preparing pure hydrogen sulphide, precipitated zinc or antimony sulphide (p. 220) is treated with hydrochloric acid; the gas is washed with water, dried with phosphorus pentoxide (not with sulphuric acid), and collected in a glass bulb (not over mercury).

As hydrogen sulphide is used so much in analytical work, its reactions with various substances should be carefully noted. These are of two types: (*a*) double decompositions leading, as a rule, to the precipitation of an insoluble sulphide (p. 220), or to the formation of a soluble sulphide (p. 267); and (*b*) reactions in which hydrogen sulphide acts as a reducing agent. Important examples of the latter are described on pp. 421, 422, 452, and 507.

A sulphur compound corresponding with hydrogen peroxide is not known, but a yellow oil of the composition H_2S_5 (?) obtained by adding a solution of calcium polysulphide † to hydrochloric acid is sometimes called *hydrogen persulphide*.

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* Papers moistened with a solution of lead acetate (p. 279) are often used in testing for hydrogen sulphide in gaseous mixtures, as they are turned brown or black by this gas owing to the formation of lead sulphide,

$$Pb(C_2H_3O_2)_2 + H_2S = PbS + 2C_2H_4O_2.$$

† Obtained by heating sulphur with milk of lime.

SULPHUR DIOXIDE, SO_2 OR $O = S = O$.

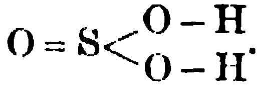
Sulphur dioxide (p. 229), like hydrogen sulphide, is a very important reducing agent, and examples of its action are given on pp. 414, 452, 482, 506, &c.

Its (unusual) oxidising action on hydrogen sulphide (p. 289) is easily demonstrated by placing cylinders containing the two gases mouth to mouth; if both gases are dry no visible action occurs, but on a few drops of water being added, sulphur is rapidly deposited on the moistened surface of the glass.

Liquid sulphur dioxide (footnote, p. 232) boils at 8° under atmospheric pressure.

In addition to sulphur trioxide (p. 231), sulphur sesquioxide, S_2O_3, and sulphur heptoxide, S_2O_7, are known. The latter is the anhydride of persulphuric acid (p. 495).

SULPHUROUS ACID, H_2SO_3 OR $O = S\begin{smallmatrix}O-H\\O-H\end{smallmatrix}$.



The only *normal* salt of sulphurous acid (p. 233) which is of much importance is **sodium sulphite**, Na_2SO_3, which is prepared by passing sulphur dioxide into a solution of sodium carbonate until carbon dioxide ceases to be evolved, and then evaporating the solution out of contact with the air,

$$Na_2CO_3 + H_2SO_3 = Na_2SO_3 + CO_2 + H_2O.$$

It forms colourless crystals, is readily soluble in water, and like all sulphites is decomposed by hydrochloric or sulphuric acid, giving sulphur dioxide,

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O;$$

consequently sodium sulphite is often used in preparing sulphur dioxide.

Sodium sulphite, both in the dry state and in aqueous solution, combines with atmospheric oxygen, giving sodium sulphate. Although it is a normal salt, its solution has an alkaline reaction to litmus.

Calcium sulphite, $CaSO_3$ (p. 234), is only sparingly soluble in water.

Sodium hydrogen sulphite, $NaHSO_3$ (p. 260), or sodium bisulphite, may be obtained in colourless crystals by passing sulphur dioxide in *excess* into a cold saturated solution of sodium carbonate, or into a concentrated solution of sodium hydroxide. It oxidises on exposure to the air, and its solution acts in most respects like that of sulphurous acid. When, for example, sodium hydrogen sulphite is added to chlorine water the halogen is reduced,

$$2NaHSO_3 + Cl_2 + H_2O = Na_2SO_3 + 2HCl + H_2SO_4 ;$$

the acids thus formed then act on the sulphite or acid sulphite, and sulphurous acid is liberated. Sodium hydrogen sulphite is used, under the name 'bisulphite-antichlor,' for removing traces of 'chlorine' from materials which have been bleached with 'chlorine' (bleaching powder, p 639). Unless the 'chlorine' is completely removed, a result which is difficult to attain by washing with water, the fabric or other material is liable to become 'tender' and fall to pieces.

Calcium hydrogen sulphite, $Ca(HSO_3)_2$, prepared by saturating milk of lime (p. 69) with sulphur dioxide, is used in the paper industry under the name of 'bisulphite of lime.' Like all acid sulphites, it is readily soluble in water.

When sulphur dioxide combines with water to give sulphurous acid, the union probably occurs in the usual manner, two hydroxyl-groups being formed from $=O$ and H_2O (p. 468). If so, the molecule of sulphurous acid would have the structure given above. The behaviour of the acid also accords with this view of its constitution, as, for example, its formation by the hydrolysis of sulphurous chloride (p 483).

Hyposulphurous acid, $H_2S_2O_4$, is produced when a saturated solution of sulphurous acid is left in contact with zinc in the cold,

$$Zn + 3H_2SO_3 = ZnSO_3 + H_2S_2O_4 + 2H_2O.$$

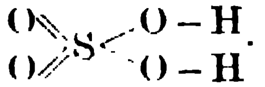
Similarly, a solution of the sulphites and hyposulphites of zinc and of sodium is obtained when zinc is left in a cold solution of sodium hydrogen sulphite. This solution is used in dyeing with indigo; it is a very active reducing agent, and rapidly absorbs oxygen on exposure to the air.

Sulphurous chloride or *thionyl chloride*, $SOCl_2$ or $O=SCl_2$, is a colourless fuming liquid (b.p. 80°) obtained by passing dry sulphur dioxide over phosphorus pentachloride, or by treating sulphites with phosphorus pentachloride,

$$PCl_5 + SO_2 = SOCl_2 + POCl_3.$$
$$2PCl_5 + Na_2SO_3 = SOCl_2 + 2NaCl + 2POCl_3.$$

It is decomposed by cold water, giving hydrochloric and sulphurous acids, and is therefore the chloride of sulphurous acid (p. 492).

SULPHURIC ACID, H_2SO_4 OR



$$\begin{matrix}O\\O\end{matrix}\!\!>\!S\!<\!\!\begin{matrix}O-H\\O-H\end{matrix}.$$

In the manufacture of sulphuric acid by the '*leaden chamber process*' (p. 287) the materials used are (1) iron pyrites, or zinc sulphide, or sulphur; (2) atmospheric oxygen; (3) water; and (4) a relatively small quantity of nitric acid.

The principle of the process is that sulphur dioxide, obtained by burning iron pyrites (pp. 221, 287), or zinc sulphide, or sulphur, in the air, is oxidised by *atmospheric* oxygen in presence of some oxide of nitrogen which acts catalytically (pp. 233, 288).[*] The sulphur trioxide thus produced combines with water vapour to form sulphuric acid.

The apparatus shown diagrammatically in fig. 102 consists of the ovens or burners (*a*, *a*), the Glover tower (*b*), the leaden chambers (*c*, *c'*), of which two only are shown, and the Gay-Lussac tower (*d*). A steam boiler, not shown, supplies steam to the pipe (*e*), and the required quantity of nitric acid is passed into the chambers in the manner described below.

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[*] In a great many processes of catalysis it is not known how the catalyst acts, and the catalyst *seems* to remain unchanged both in quantity and in composition during the reaction. Hence the terms catalysis and catalyst rather imply these conditions. Since in the preparation of sulphuric acid it is known that the oxide of nitrogen is chemically changed, and that a considerable proportion of it may at any given time be present in a combined form, it is doubtful whether or not the oxide should be spoken of as a catalyst. Similarly in other cases.

In the ovens (*a*, *a*) iron pyrites, zinc sulphide, or sulphur is burnt on shelves in an *excess* of air. The combustion of zinc sulphide and of poor qualities of pyrites must be assisted by fires, but good pyrites and sulphur continue to burn by themselves when once ignited. The gases from the burners pass through flues, in which dust is deposited, and then enter at the bottom of the Glover tower, together, as a rule, with nitric acid vapour.

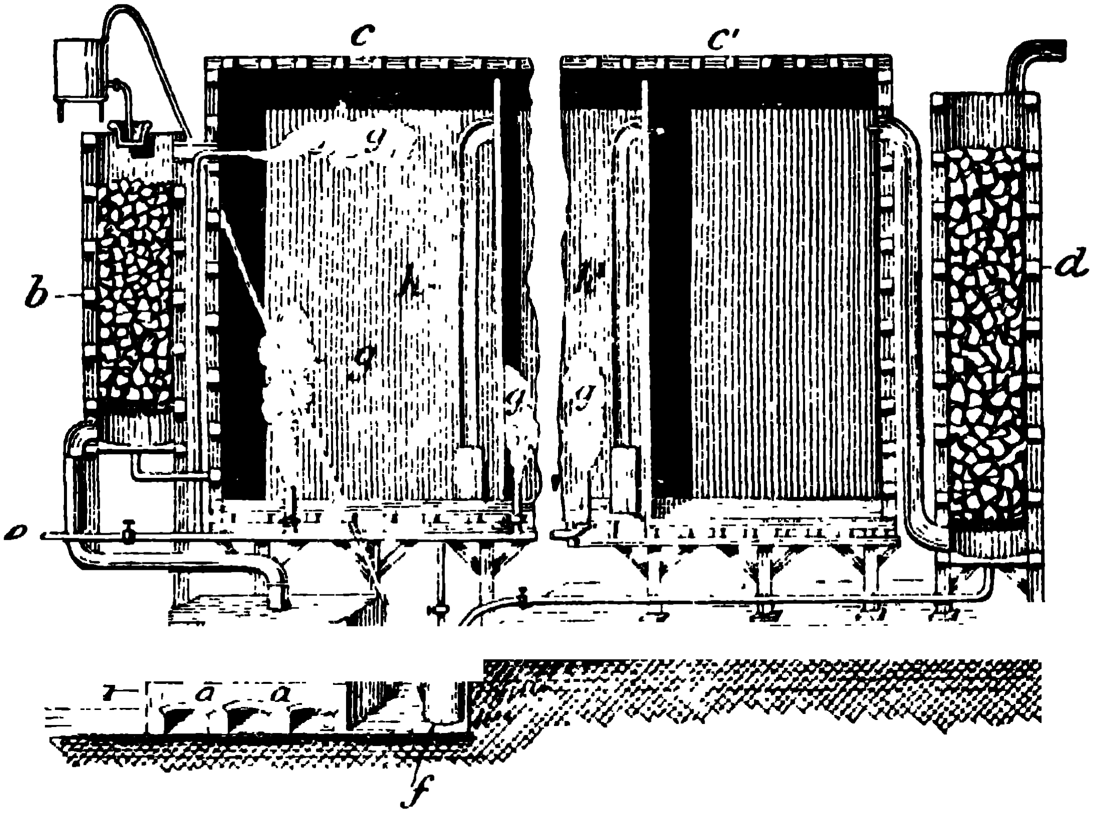

Fig. 102.

The Glover tower (*b*) consists of a cylindrical or rectangular chamber of sheet-lead (supported by a wooden framework) filled with flints or with very small hollow earthenware cylinders. Sulphuric acid from the Gay-Lussac tower (*d*) and dilute acid (‘*chamber acid*’) from the chambers are forced by air-pressure from the vessel (*f*) to the top of the Glover tower, and after passing through a distributor the mixture trickles down through the contents of the tower, meeting the ascending hot gases from the ovens (*a*, *a*). The results are: (1) The sulphuric acid from the Gay-Lussac tower gives up the oxides of nitrogen which it has absorbed (see below); (2) the acid from the chamber is concentrated, and the water which it loses is returned to the chambers; (3) the furnace gases are cooled. In some works the nitric acid required in the chambers is added to the sulphuric acid which is run down the Glover tower, but in others a mixture of sodium nitrate and sulphuric acid is heated in pans placed near the pyrites ovens, and the sulphur dioxide passes over these pans, carrying the reduction products of the nitric acid to the Glover tower.

The sulphur dioxide and the reduction products of the nitric acid, together with a large volume of atmospheric gases, enter the first chamber (*e*), where they mix with steam from the pipes (*g*, *g*). The gases then pass up the pipe (*h*) into the second, and up the pipe (*h'*) into the third chamber, and enter at the bottom of the Gay-Lussac tower (*d*), from the top of which they escape through a tall chimney into the air.

The Gay-Lussac tower (*d*), constructed like the Glover tower, is also provided with a distributor, from which *concentrated* sulphuric acid flows down the tower. This acid absorbs oxides of nitrogen from the chamber gases (see below) and runs into the vessel (*f*), from which it is forced to the top of the Glover tower. In this tower it gives up the oxides of nitrogen.

The chambers (*e*, *e'*) are made of sheets of pure lead* melted together at their edges; they are supported on a wooden framework, to which the walls and roof of the chamber are fastened by means of strips of lead. The capacity of a chamber is sometimes 200,000 cubic feet.

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* Unless the lead is pure it is corroded by the acid; but lead which contains a very small proportion of antimony, and which is much harder than pure lead, may also be employed. The pure metal must be used for the construction of the leaden evaporating-pans.

The acid which collects at the bottom of the chambers contains only 60 to 70 per cent. of hydrogen sulphate, and for many purposes has to be concentrated by evaporating away the water. The first stages of this concentration are carried out in pans lined with lead, but as the stronger acid attacks this metal, glass, or platinum, or silica vessels must be used in the later stages.

The reactions which may occur in the formation of sulphuric acid have already been indicated (p. 287), but other explanations have been suggested.

According to Lunge, the principal reactions, after the nitric acid has once been reduced to nitrous acid, consist in the formation of *nitrosylsulphuric acid*, with fixation of atmospheric oxygen,

$$2SO_2 + 2HNO_2 + O_2 = 2SO_2(O{\cdot}NO)OH.$$

and the decomposition of this compound by water, with regeneration of the whole of the original quantity of nitrous acid,

$$2SO_2(O{\cdot}NO)OH + 2H_2O = 2H_2SO_4 + 2HNO_2.$$

In support of this view there is the fact that when the supply of steam is insufficient, colourless crystals (chamber crystals) of nitrosylsulphuric acid are deposited on the walls of the chamber.*

The object of the Gay-Lussac tower (*d*) is to prevent the valuable oxides of nitrogen from being carried away by the large volume of atmospheric gases leaving the chamber. Concentrated sulphuric acid absorbs nitrogen tetroxide, N_2O_4 (or its dissociation product, NO_2, p. 350), with formation of nitrosylsulphuric acid,

$$H_2SO_4 + 2NO_2 = SO_2(O{\cdot}NO)OH + HNO_3.$$

*** The reduction of nitric acid and the production of this crystalline compound may be easily demonstrated by passing sulphur dioxide into a flask which is moistened all over the inside with fuming nitric acid.**

This compound dissolves in the strong acid, but when its solution is mixed with dilute chamber acid and passed down the Glover tower, it is decomposed by the water of the dilute acid and by the sulphur dioxide,

$$2SO_2(O{\cdot}NO)OH + SO_2 + 2H_2O = 3H_2SO_4 + 2NO,$$

and the liberated nitric oxide is carried back to the chamber.

As nitric oxide is not absorbed by sulphuric acid, the gases escaping from the last chamber must always contain oxygen sufficient to convert the whole of the nitric oxide into higher oxides of nitrogen, otherwise great loss occurs. Even under the most favourable circumstances a small proportion of the nitric acid is finally converted into nitrous oxide or into nitrogen, and as these reduction products are useless, and escape into the atmosphere, the acid must be added continuously in small quantities to compensate for loss.

Commercial *oil of vitriol* (O.V.) made by the above process has a specific gravity of about 1·84 at 15°, and contains about 93 to 96 per cent. of hydrogen sulphate. In addition to water, it often contains impurities such as lead sulphate, arsenious oxide, oxides of nitrogen, and dissolved mineral matter. The brown colour sometimes seen is due to the presence of charred vegetable matter, such as straw.

When the commercial acid is diluted with 10-20 volumes of water, a deposit of lead sulphate may be slowly formed; this salt is much more soluble in the strong acid (probably as lead hydrogen sulphate) than in the dilute. The presence of arsenic compounds may be detected by Marsh's test (p. 551); the presence of oxides of nitrogen, by boiling the diluted acid and testing the escaping aqueous vapour with a starch-potassium-iodide paper (p. 416).

Commercial sulphuric acid may be freed from dissolved mineral matter, including lead sulphate, by distillation, but the distilled acid may still contain arsenious oxide, from which the (crude) acid may be freed by adding to it a little barium sulphide, this substance converts the arsenious oxide into the insoluble sulphide, with formation also of insoluble barium sulphate.

In the manufacture of sulphuric acid by the *contact process* (p. 232), sulphur dioxide, prepared by the methods above described, is combined with atmospheric oxygen in presence of finely divided platinum.* This reaction only takes place rapidly when the mixture is heated, and is accompanied by a very considerable development of heat, in consequence of which a very high temperature may be reached unless precautions are taken. Now, as the reaction is a reversible one, and sulphur trioxide is decomposed at high temperatures, unless the temperature is very carefully regulated the combination of the sulphur dioxide and oxygen is very incomplete.

The process based on these principles is carried out in the apparatus shown diagrammatically in fig. 103.

The iron cylinder (*a*) contains a number of tubes (*b*) filled with platinised asbestos, which is supported at intervals by perforated plates. These tubes pass through the iron plates (*c*, *c*), and thus connect the chambers (*d*, *d'*). The cold mixture of sulphur dioxide and atmospheric gases, carefully dried with the aid of sulphuric acid, is led into the iron cylinder from the pipes (*e*, *f*, *g*), the supply from each of which can be regulated by valves. The supply from (*e*) and (*f*) passes upwards through the spaces between the tubes (*b*), and *cools* these tubes to the desired temperature. The ascending gaseous mixture is thus *heated*, so that by the time it enters the chamber (*d*) and has been mixed, if necessary, with cold gases entering from the pipe (*g*), it has acquired the requisite temperature.

At the commencement of the process the contact chamber is heated by means of the burners (*i*, *i'*), the products of combustion escaping through the flue (*j*); but afterwards the chamber is maintained at a constant temperature (about 430°) in the manner just described.

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* Ferric oxide, the residue obtained on roasting pyrites, is also used as a catalytic agent in some works.

The sulphur trioxide, which escapes in the form of vapour from the tubes (*b*) into the chamber (*d'*), passes through

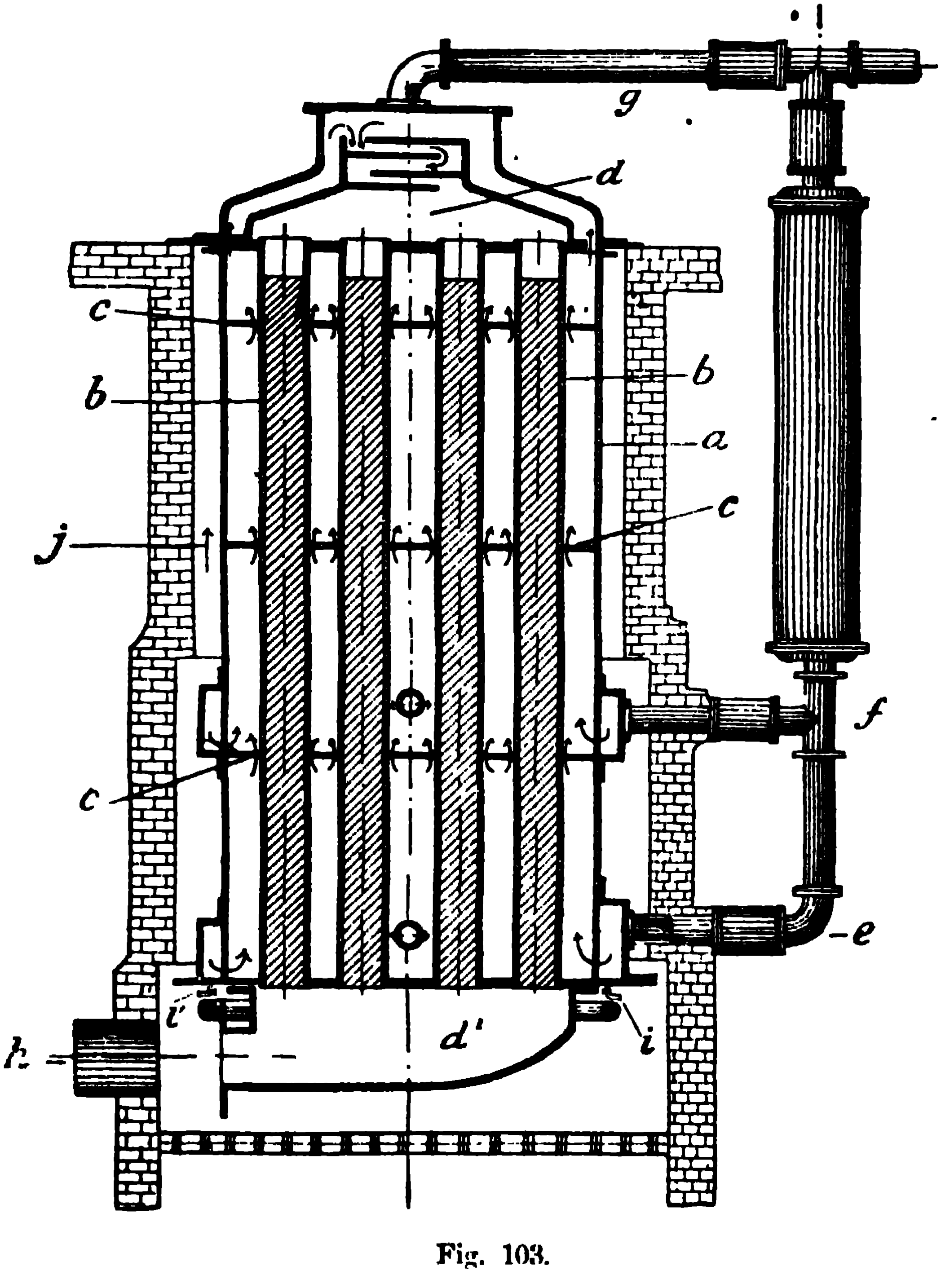

Fig. 103.

the outlet (*h*), and is absorbed in concentrated sulphuric acid. The solution thus obtained is used directly (see disulphuric acid, p. 493), or is continuously diluted with water sufficient to form sulphuric acid by combination with the anhydride.

The product is of a very high degree of purity, because, unless the gases are most carefully purified and freed from dust, the catalytic action of the platinum rapidly falls off.

Sulphuric acid is used in large quantities in the manufacture of nitric acid, hydrochloric acid, sulphurous acid, carbonic acid, sodium carbonate, superphosphates (p. 550), alums (p. 616), and explosives, and in the colour industry; in smaller quantities for a great many other purposes.*

Sulphuric acid dissociates when it is heated, and at 440° the change is practically complete under atmospheric pressure,

$$H_2SO_4 \longleftrightarrow SO_3 + H_2O.$$

At still higher temperatures it gives sulphur dioxide, oxygen, and water. It sometimes acts as an oxidising agent, thus it oxidises hydrogen sulphide at ordinary temperatures,

$$H_2SO_4 + H_2S = SO_2 + 2H_2O + S.$$

As a rule, however, it only oxidises substances at moderately high temperatures, as in the case of sulphur and carbon (p. 231).

Owing to the occurrence of thermal dissociation the molecular weight of sulphuric acid cannot be established by determining the vapour density, and owing to the occurrence of ionic dissociation (p. 391) the molecular weight cannot be determined in aqueous solution. That the molecular formula of the acid is very probably H_2SO_4 is shown, however, by the results of vapour density determinations made with simple derivatives of sulphuric acid, such as sulphuryl chloride, SO_2Cl_2, or dimethyl sulphate, $(CH_3)_2SO_4$.†

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* Sulphuric acid is used in the manufacture of so many other substances that the state of all the other chemical industries of a country may be roughly gauged by the quantity of sulphuric acid which that country utilises.

† At ordinary temperatures the molecules, H_2SO_4, are probably associated (compare water, p. 467).

The Sulphates.—Many normal sulphates have already been described. One of the more important classes of normal salts is that known as the vitriol class, which includes those sulphates of bivalent metals which crystallise with $7H_2O$. Thus the salts $FeSO_4, 7H_2O$; $ZnSO_4, 7H_2O$; $MgSO_4, 7H_2O$, belong to this class, and are isomorphous (p. 321). Copper sulphate, $CuSO_4, 5H_2O$, although commonly known as 'blue vitriol,' is not a member of the vitriol class.

Several types of *double sulphates* are known: of these, the alums (p. 616) have already been mentioned (p. 295). Another important class is that represented by *ferrous ammonium sulphate*. When a solution of approximately equivalent quantities of ferrous sulphate and ammonium sulphate is crystallised, the double salt $FeSO_4, (NH_4)_2SO_4, 6H_2O$ separates in pale-green crystals. Many other salts of this type are known, as the sulphates of zinc, magnesium, and some other bivalent metals may take the place of the ferrous sulphate, and those of potassium and some other univalent metals may take the place of the ammonium sulphate in this double salt. The double salts of this type, therefore, may be represented by the general formula $M''SO_4, M'_2SO_4, 6H_2O$, where M'' stands for certain bivalent metals, and M' for certain univalent metals or univalent basic radicles (p. 266).

Acid sulphates, of which the best known are *sodium hydrogen sulphate* (p. 258) and potassium hydrogen sulphate, $KHSO_4$, are decomposed at high temperatures, first giving di- or pyro-sulphates, and finally normal salts,

$$2NaHSO_4 = Na_2S_2O_7 + H_2O, \qquad Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

Barium sulphate, although insoluble in water, dissolves in concentrated sulphuric acid, probably owing to the formation of *barium hydrogen sulphate*, $Ba(HSO_4)_2$; similarly with the sulphates of strontium, calcium, and lead.

Chlorosulphonic acid, $SO_2Cl(OH)$, is formed by the combination of sulphur trioxide and dry hydrogen chloride; also by treating pure sulphuric acid with one molecular proportion of phosphorus pentachloride,

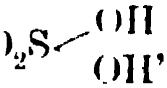
$$H_2SO_4 + PCl_5 = SO_2Cl(OH) + POCl_3 + HCl.$$

The product is purified by fractional distillation, and is obtained as a colourless fuming liquid (b.p. 156°), which is decomposed by water, giving sulphuric and hydrochloric acids.

Sulphuryl chloride, SO_2Cl_2, is formed when a mixture of chlorine and sulphur dioxide is exposed to direct sunlight. It is a colourless fuming liquid (b.p. about 70°), and is decomposed by water, with formation of sulphuric and hydrochloric acids.

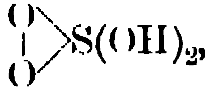
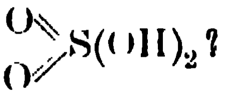
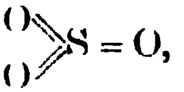
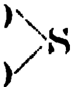
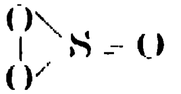
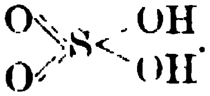
Acid Chlorides.—Compounds such as sulphuryl chloride and chlorosulphonic acid, which are derived from acids by the displacement of one or more hydroxyl-groups by an equivalent quantity of chlorine, are termed acid chlorides or chloranhydrides.

Constitution of Sulphuric Acid.—In order to determine the structure or constitution of a compound it is necessary not only to consider the valencies of the elements in the molecule of that compound, but also to examine the chemical behaviour of the compound and that of as many of its derivatives as possible.

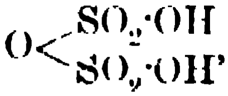
Now sulphuric acid is formed by the direct union of sulphur trioxide and water. From the study of the change which generally occurs when an oxide unites with water (p. 468), it would seem that in this union the molecules of $O_2S:O$ and H_2O give molecules  $O_2S{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$, in which case the molecule of sulphuric acid contains two hydroxyl-groups. This view is confirmed by the fact that sulphuric acid is a dibasic acid, because, from the behaviour of oxygen acids as a class, it is concluded that their *displaceable* hydrogen atoms are directly united with oxygen.

The formation of sulphuric and hydrochloric acids by the hydrolysis of sulphuryl chloride affords further evidence in support of this view, since this reaction cannot well be explained except by assuming that it consists in the simple displacement of each of the univalent chlorine atoms by a univalent hydroxyl-group.

A study of the relation of sulphuric acid to sulphurous acid, disulphuric acid, and to many other compounds also leads to the formula $SO_2(OH)_2$.

The question next arises, what is the valency of sulphur in sulphuric acid? Is the element quadrivalent as represented in the formula  $\begin{matrix}O\\|\\O\end{matrix}\!>\!S(OH)_2$, or sexvalent as represented in the formula  $\begin{matrix}O\\O\end{matrix}\!\gg\!S(OH)_2$? This question is more difficult to answer. As there are no reasons for supposing that the oxygen atoms in sulphur dioxide and sulphur trioxide are directly united with one another, the structures of these compounds are represented by the formulæ $O=S=O$ and  $\begin{matrix}O\\O\end{matrix}\!\gg\!S=O$, and not by  $\begin{matrix}O\\|\\O\end{matrix}\!>\!S$ and  $\begin{matrix}O\\|\\O\end{matrix}\!>\!S-O$ respectively. From analogy, and because there is no evidence to the contrary, the two oxygen atoms, which in the molecule of sulphuric acid are not united with hydrogen, are represented as being united to the sulphur atom only, and not to one another as well as to sulphur. For these and other reasons it is supposed that sulphur is sexvalent in sulphuric acid, and that the acid has the constitution  $\begin{matrix}O\\O\end{matrix}\!\gg\!S\!<\!\begin{matrix}OH\\OH\end{matrix}$.

Aqueous solutions of sulphuric acid probably contain the molecules $O=S(OH)_4$ and $S(OH)_6$, which are produced by the combination of the H_2SO_4 molecules with H_2O and $2H_2O$ respectively.

Disulphuric acid, $H_2S_2O_7$ or  $O\!<\!\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}$, is obtained in

an impure state when hydrated ferrous sulphate (green vitriol) is heated alone (p. 39), or with silica. The salt first loses water and then decomposes, and finally sulphur trioxide volatilises. If the whole of the distillation products are collected together, dilute 'oil of vitriol' or sulphuric acid is obtained; but if the receiver is changed when the salt has been almost completely dehydrated, the distillate then collected is a strongly fuming liquid.

The fuming product was formerly prepared at Nordhausen, and thus came to be known as *Nordhausen* sulphuric acid or *fuming* sulphuric acid. It is a solution of *disulphuric acid* in sulphuric acid.

The changes which occur in the preparation of this impure acid depend on the nature of the material employed. If green vitriol crystals ($FeSO_4, 7H_2O$) are used, the salt first loses most of its water; some of the ferrous sulphate then decomposes, giving ferric oxide, sulphur trioxide, and sulphur dioxide,

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3,$$

and the sulphur trioxide thus formed oxidises some of the ferrous sulphate to a *basic* ferric sulphate,

$$2FeSO_4 + SO_3 = Fe_2O(SO_4)_2 + SO_2.$$

The basic ferric sulphate in the later stages decomposes, giving ferric oxide and sulphur trioxide,

$$Fe_2O(SO_4)_2 = Fe_2O_3 + 2SO_3.$$

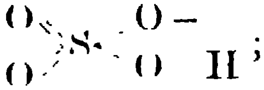
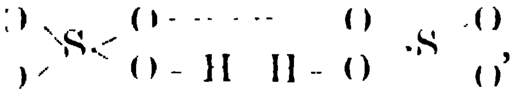
In practice the green vitriol is generally first roasted in the air at a low temperature; it then loses most of its water, and is oxidised to a basic ferric sulphate, $Fe_2O(SO_4)_2$ or $Fe_2O_3, 2SO_3$ (known as *vitriol stone*), which decomposes into ferric oxide and sulphur trioxide when it is submitted to destructive distillation. A *portion* of the sulphur trioxide combines with water from the original material to form sulphuric acid, which dissolves the remainder of the trioxide. The residue of ferric oxide is sold as '*rouge*' or *Venetian red*.

Disulphuric acid may be obtained in colourless crystals (m.p. 35°) by dissolving sulphur trioxide (obtained by the contact process) in sulphuric acid, and then cooling the solution. It may be regarded as an *anhydride* of sulphuric acid,

$$2H_2SO_4 = H_2S_2O_7 + H_2O,$$

and is often called *anhydrosulphuric acid*. As its salts are formed by heating acid sulphates (p. 491), it is also known as *pyrosulphuric acid*.

Disulphuric acid and its salts combine with water, the acid giving sulphuric acid, and the salts acid sulphates. The acid is used in the colour industry.

Potassium persulphate, $K_2S_2O_8$, is deposited in crystals when a saturated solution of potassium hydrogen sulphate is submitted to electrolysis under suitable conditions. The formation of this salt is due to secondary reactions. The primary products of electrolysis are atoms of potassium and univalent radicles,  $\begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}O-\\O-H\end{matrix}$; but when the latter are liberated at the anode they unite to form **persulphuric acid,**  $\begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}O-\!-\!-\!-\!-\!-O\\O-H\quad H-O\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix}$, and this acid then reacts with some of the potassium hydrogen sulphate to form the sparingly soluble potassium salt. The same salt is formed when a solution of potassium sulphate is used, and similarly *sodium persulphate* and *ammonium persulphate* are obtained by the electrolysis of solutions of the corresponding sulphates.

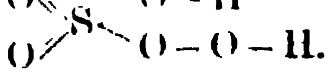
The persulphates decompose when they are gently heated, giving disulphates and oxygen,

$$2K_2S_2O_8 = 2K_2S_2O_7 + O_2;$$

and in aqueous solution they are active oxidising agents, as they decompose readily, liberating oxygen (and ozone),

$$2Na_2S_2O_8 + 2H_2O = 2Na_2SO_4 + 2H_2SO_4 + O_2.$$

Persulphuric acid (or per*di*sulphuric acid) is formed when pure hydrogen dioxide is carefully added to sulphur trioxide ($H_2O_2 + 2SO_3 = H_2S_2O_8$), Caro's acid being produced as an intermediate product.

Per*mono*sulphuric acid (Caro's acid) is a monobasic acid, of the constitution  $\begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}O-H\\O-O-H\end{matrix}$.

It is formed when pure sulphuric acid is treated with pure hydrogen peroxide,

$$H_2SO_4 + H_2O_2 = H_2SO_5 + H_2O,$$

but is best prepared by adding pure hydrogen peroxide to well-cooled chlorosulphonic acid; it forms colourless crystals and melts at about 45°. A mixture made from sulphuric acid and a persulphate, or a peroxide, is known as *Caro's reagent*, and is used as an oxidising agent.

THIOSULPHURIC ACID, $H_2S_2O_3$ OR $SO_2{<}^{OH}_{SH}$.

The name *thiosulphuric acid*, now given to an acid formerly called hyposulphurous acid, signifies sulphur sulphuric acid (Greek, *theion* = sulphur), and was chosen because theoretically thiosulphuric acid is derived from sulphuric acid by displacing one atom of oxygen by one atom of sulphur.

The sodium salt of this acid is formed when a solution of sodium sulphite is boiled with excess of sulphur, just as sodium sulphate is produced when the sulphite is exposed to oxygen,

$$Na_2SO_3 + S = Na_2S_2O_3;$$

when the filtered solution is concentrated and cooled, hydrated **sodium thiosulphate,** $Na_2S_2O_3, 5H_2O$, is deposited in crystals.

Sodium thiosulphate is also formed when sulphur dioxide is passed into a solution of sodium sulphide, and when a solution of sodium polysulphide is exposed to the air. In the former case sodium sulphite and hydrogen sulphide are first formed,

$$Na_2S + H_2SO_3 = Na_2SO_3 + H_2S,$$

and the hydrogen sulphide is then decomposed by more sulphur dioxide, giving water and sulphur; the thiosulphate is then produced by the reaction given above. When sodium polysulphide is exposed to the air, the final results may be expressed by the equation,

$$2Na_2S_5 + 3O_2 = 2Na_2S_2O_3 + 6S.$$

Sodium thiosulphate is very readily soluble in hot water, and its aqueous solutions show the phenomenon of supersaturation (p. 312) in a striking manner. A hot, nearly saturated solution which has been cooled to ordinary temperatures, the usual precautions having been taken, immediately begins to crystallise when it is seeded, and the process continues until most of the solution is changed into a mass of the hydrated salt.

Solutions of sodium thiosulphate and of iodine react very readily, with formation of sodium iodide and sodium tetrathionate (p. 498),

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

This reaction is an important one, as it is used in the laboratory for estimating the quantity of *iodine* in a solution.

For this purpose a *standard* solution of sodium thiosulphate (a $\frac{N}{10}$ solution contains $\frac{1}{10}$ gram-molecule per litre, because 1 molecule $Na_2S_2O_3$ = 1 atom of iodine) is run from a burette into the solution of iodine, which has been previously mixed with a little starch solution; the end point is reached when the deep-blue colour of the solution (p. 415) just disappears.

Many of those substances which oxidise hydrogen iodide (p. 423) may be estimated with the aid of thiosulphate; thus the percentage of chlorine in a sample of chlorine water may be determined by adding a weighed or measured quantity of the liquid to a solution of excess of potassium iodide, and then estimating the liberated iodine as described above.

The quantity of manganese dioxide, lead dioxide, red-lead, potassium chromate, potassium dichromate, &c. in samples of the impure materials may also be estimated with the aid of sodium thiosulphate. The sample is heated with excess of hydrochloric acid, and the evolved chlorine is passed into a solution of potassium iodide; if the sample is soluble in water, it is merely added to excess of an acidified solution of potassium iodide. The liberated iodine is then titrated with sodium thiosulphate.

The action of chlorine (and of bromine) on a solution of sodium thiosulphate is very different from that of iodine, and may be expressed by the equation,

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = 2NaHSO_4 + 8HCl.$$

Sodium thiosulphate is used as an 'antichlor' (p. 482) for removing 'chlorine' from bleached fabrics.

Solutions of sodium thiosulphate give with silver chloride, bromide, or iodide the *soluble* salt, **sodium silver thiosulphate,** and the sodium salt of the halogen acid,

$$Na_2S_2O_3 + AgCl = NaAgS_2O_3 + NaCl.$$

Owing to this fact sodium thiosulphate is used in photography (under the name of 'hypo') in the fixing process, that is to say, in dissolving the unchanged silver halide and leaving the insoluble substance which has been formed from it by the action of light.

When an acid is added to a solution of any thiosulphate, sulphur dioxide is evolved, and after a short time a precipitate of sulphur is formed, because when thiosulphuric acid is liberated from its salts it undergoes decomposition spontaneously,

$$H_2S_2O_3 = SO_2 + S + H_2O.$$

This behaviour serves for the detection of thiosulphates.

Potassium thiosulphate resembles the sodium salt. **Barium thiosulphate,** BaS_2O_3, is only sparingly soluble in water.

Thionic Acids.—**Tetrathionic acid,** $HO{\cdot}SO_2{\cdot}S{\cdot}S{\cdot}SO_2{\cdot}OH$, is obtained in the form of its sodium salt when sodium thiosulphate is treated with iodine in aqueous solution (see above), the barium salt, prepared in a similar manner from barium thiosulphate, may be obtained free from barium iodide, by fractional crystallisation from aqueous alcohol, and from this salt a solution of tetrathionic acid may then be produced (footnote, p. 433). Tetrathionic acid is a colourless liquid; it easily decomposes, giving sulphuric and sulphurous acids, together with sulphur.

Several other 'thionic' acids are known in the form of their salts. **Dithionic acid,** $H_2S_2O_6$, for example, is obtained, as manganese dithionate, by passing sulphur dioxide into water which contains hydrated manganese dioxide (p. 416) in suspension. The reaction is doubtless a complex one, and the formation of the manganese dithionate is probably the result of a reduction of manganic sulphate, as shown by the partial equation,

$$Mn_2(SO_4)_3 = MnS_2O_6 + MnSO_3 + 3O$$

Manganese dithionate is also formed in small quantities when potassium permanganate is reduced with sulphurous acid in the cold.

Selenium, Se_2(?), at. wt. 79·2, occurs in very small quantities in some samples of native sulphur, and also (in the place of sulphur) in some samples of iron pyrites. It was discovered by Berzelius in a deposit from some sulphuric acid chambers, and is known in two or three allotropic forms. One of these is a red amorphous solid (sp. gr. 4·26) obtained by reducing a cold solution of selenious acid with sulphurous acid; this form is soluble in carbon disulphide (from which it separates in red crystals), but when it is heated at about 120° it is quickly transformed into a gray crystalline modification (metallic selenium) of sp. gr. 4·8, which is insoluble in carbon disulphide. Metallic selenium melts at 217°; it is a conductor of electricity, and its conductivity is greater in the light than in the dark.

Hydrogen selenide, H_2Se, is obtained as a gas when ferrous selenide is treated with concentrated hydrochloric acid; it is very similar to hydrogen sulphide, but is more readily soluble in water and has a more offensive smell than the sulphide.

Selenium dioxide, SeO_2, is formed when selenium is burnt in the air; it is crystalline, sublimes when heated, and combines with water to form selenious acid.

Selenious acid, H_2SeO_3, is crystalline; it is easily reduced to selenium in aqueous solution, and is oxidised by chlorine or bromine, giving **selenic acid,** H_2SeO_4 (m.p. 58°). When selenic acid is heated with hydrochloric acid it is reduced to selenious acid, and when heated alone it is decomposed into water, oxygen, and selenium dioxide. The *anhydride*, SeO_3, is unknown.

Tellurium, Te_2, at. wt. 127·5, occurs in the free state, and in combination with gold and silver; it was discovered by Müller von Reichenstein, and is known in an amorphous and in a crystalline modification. The former, a black powder of sp. gr. 6·0, is obtained by reducing tellurious acid with sulphurous acid; the latter, a silvery substance of sp. gr. 6·2 and m.p. 452°, is obtained by melting the amorphous modification and then cooling the liquid.

Hydrogen telluride, H_2Te, **tellurium dioxide,** TeO_2, and **tellurious acid,** H_2TeO_3, may be prepared by methods similar to those used in obtaining the corresponding selenium compounds, which they resemble respectively in properties.

Telluric acid, H_2TeO_4, is obtained in the form of its potassium salt by fusing tellurium or its dioxide with potassium nitrate. The *anhydride*, TeO_3, is obtained as a yellow solid by heating the acid; it is insoluble in water.

THE RELATIONSHIP OF THE ELEMENTS OF THE OXYGEN SUB-FAMILY.

In this sub-family, which comprises oxygen, sulphur, selenium, and tellurium, the relationship is on the whole similar to that in the halogen sub family.

The physical properties show a gradual change with increasing atomic weight, as indicated by the following data:

	Oxygen.	Sulphur.	Selenium.	Tellurium.
M.p. . .	−230°	+114°	+217°	+452°
B.p. . .	−181°	+448°	+680°	red heat.

With regard to chemical properties, the matter is to some extent confused by the fact that the more important compounds of sulphur, selenium, and tellurium are those which they form with oxygen, and which therefore cannot be compared with any corresponding derivatives of that element.

Oxygen, indeed, in some respects, occupies a unique position in the sub-family, and its properties differ from those of the other members, just as those of fluorine differ from those of the other three halogens. Thus the hydride of oxygen, H_2O, is a liquid at ordinary temperatures (p. 467) and is not acidic, whereas hydrogen sulphide is a gas and has distinctly acid properties. Nevertheless the relationship between oxygen and sulphur is clearly shown by the fact that with nearly all the metals these two elements yield compounds of the same type, while corresponding oxides and sulphides are on the whole very similar in properties. The relationship is even more strikingly illustrated by a comparison of some of the more complex derivatives of these two elements, as, for example, the arsenites and thioarsenites, the arsenates and thioarsenates (p. 567), and so on.

The relationship between sulphur, selenium, and tellurium is perhaps even closer than that between oxygen and sulphur. These three elements form compounds of the same type, and in any set of corresponding compounds, while the chemical properties are very much the same, both the physical and the chemical properties show a graded change in passing from sulphur to tellurium. Thus all three elements combine with hydrogen to form compounds in which they are bivalent. These hydrides are all gaseous and show acidic properties, which become weaker as the molecular weight increases. The oxides of the type XO_2, in which the elements are quadrivalent, are all anhydrides from which the corresponding dibasic acids, H_2XO_3, are derived; the latter become less acidic with increasing molecular weight, and in fact the oxide TeO_2 may even act as a basic oxide towards strong acids. The acids of the type H_2XO_4, in which the elements are sexvalent (p. 493), are also similar in properties, but telluric acid is a very weak acid.

Corresponding solid compounds of these three elements are generally isomorphous.

CHAPTER L.

Chromium and its Compounds.

CHROMIUM, Cr;* AT. WT. 52·1.

The metal chromium, which is related, although distantly, to oxygen and sulphur, is found in nature in the form of *chrome iron stone* or *chromite*, a gray, very hard mineral, which is the principal source of chromium and all its compounds.

The metal may be obtained by reducing chromium sesquioxide (p. 511) with aluminium as described in the preparation of manganese by Goldschmidt's process (p. 443). By using a slight excess of the oxide, chromium is obtained free from aluminium as a hard, very lustrous, silvery-gray solid, of sp. gr. about 6·9, which melts only at the temperature of the electric furnace; it dissolves chemically in hot hydrochloric acid, liberating hydrogen and giving a green solution of chromic chloride.

Chrome iron stone consists principally of *ferrous chromite*, $Fe(CrO_2)_2$ or FeO, Cr_2O_3 and is used on the large scale for the preparation of potassium dichromate. For this purpose the finely ground ore is mixed with a suitable quantity of potassium carbonate, and the mixture is heated in a reverberatory furnace (p. 587) through which there passes a continuous stream of air. At the end of some hours the yellow product is cooled and treated with water; the aqueous solution thus obtained contains the salt, *potassium chromate*, K_2CrO_4, while an insoluble deposit of ferric oxide remains.

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* The molecular formula of chromium is not known.

The reactions which occur in these operations are summarised in the equation,

$$4Cr_2O_3,FeO + 8K_2CO_3 + 7O_2 = 8K_2CrO_4 + 8CO_2 + 2Fe_2O_3.$$

The principles of the process are, (*a*) the ferrous chromite is transformed into potassium chromite,

$$Fe(CrO_2)_2 + K_2CO_3 = 2KCrO_2 + FeO + CO_2,$$

and (*b*) the potassium chromite is converted by atmospheric *oxidation* in presence of alkali into potassium chromate,

$$4KCrO_2 + 2K_2CO_3 + 3O_2 = 4K_2CrO_4 + 2CO_2.$$

At the same time the ferr*ous* is oxidised to ferr*ic* oxide.

The solution of the chromate is next treated with sulphuric acid, whereby the chromate is converted into the more sparingly soluble dichromate,

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The liquid is then evaporated, and the *potassium dichromate*, which separates from the solution on cooling (leaving potassium sulphate in the mother-liquor), is purified by recrystallisation from hot water.

Sodium chromate is generally manufactured instead of the potassium salt, because sodium carbonate is very much cheaper than potassium carbonate.

The warm *concentrated* solution of the sodium chromate is then treated with sulphuric acid; in this case sodium sulphate is precipitated, and the more readily soluble sodium dichromate does not crystallise out until the solution has been further concentrated and then cooled

The sodium dichromate is then transformed into the potassium salt by treating it with commercial potassium chloride (p. 676) in hot concentrated aqueous solution. On the solution being cooled, the reversible reaction,

$$Na_2Cr_2O_7 + 2KCl \longleftrightarrow K_2Cr_2O_7 + 2NaCl,$$

proceeds from left to right, because, as the potassium dichromate is only sparingly soluble, the solution is saturated with it, and it is precipitated in crystals.

It is also very advantageous to add some quicklime before heating the mixture of chrome iron stone and alkali carbonate, because the latter melts at the high temperature employed, whereas quicklime does not; the mixture is thus rendered more porous, and in consequence the absorption of atmospheric oxygen is more rapid. When calcium oxide is employed it is finally converted into calcium carbonate, which remains with the insoluble ferric oxide, but some calcium chromate may be present in solution; in such cases the solution is boiled with sodium carbonate in order to form sodium chromate and insoluble calcium carbonate.

Potassium dichromate, $K_2Cr_2O_7$, is a red crystalline salt, and is much more soluble in hot than in cold water (its solubility is 8 at 10°, about 96 at 100°), so that it is easily recrystallised and obtained in a pure condition; this is one of the reasons why it is made the starting-point in the preparation of chromium compounds. It is a salt of **dichromic acid,** $H_2Cr_2O_7$, a substance which is derived from **chromic acid,** H_2CrO_4,

$$2H_2CrO_4 = H_2Cr_2O_7 + H_2O.$$

In the conversion of the chromate into the dichromate by the action of sulphuric acid (or other acids), it may be supposed that potassium hydrogen chromate is first formed, just as potassium hydrogen sulphate is produced from normal potassium sulphate,

$$2K_2CrO_4 + H_2SO_4 = 2KHCrO_4 + K_2SO_4,$$

and that two molecules of this salt then immediately combine together, with elimination of one molecule of water,*

$$2KHCrO_4 = K_2Cr_2O_7 + H_2O.$$

When a concentrated aqueous solution of potassium dichromate is carefully mixed with a suitable quantity of concentrated sulphuric acid and the solution is cooled, long dark-red crystals of **chromic anhydride,** CrO_3, are deposited,

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* Hence the conversion of a chromate into a dichromate is not a process of oxidation: both acids are derived from the anhydride, CrO_3.

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

The crystals may be separated by filtration through glass-wool, washed with nitric acid, and dried on unglazed earthenware.

Chromic anhydride is readily soluble in water, giving a solution of chromic acid (or of dichromic acid), just as sulphuric anhydride gives sulphuric acid, but the acid is unstable. The anhydride decomposes at about 250°, giving oxygen and chromium sesquioxide, $4CrO_3 = 2Cr_2O_3 + 3O_2$; it is a very vigorous oxidising agent, and attacks paper, alcohol, and many other compounds.

A solution of chromic acid is also a vigorous oxidising agent, and as such a solution is obtained when potassium chromate or potassium dichromate is mixed with sulphuric acid, both these salts, but especially the latter, are used for oxidising purposes.

In all such reactions the chromic acid undergoes reduction, with formation of oxygen and chromic hydroxide, as represented in the partial equation,

$$2H_2CrO_4 + H_2O = 3O + 2Cr(OH)_3,$$

but both these primary products immediately undergo change; the oxygen oxidises the reducing agent present, and the chromium hydroxide, which is a basic hydroxide, forms the corresponding sulphate with the sulphuric acid contained in the solution,

$$2Cr(OH)_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O.$$

During these changes, which generally take place rapidly at ordinary temperatures, the colour of the solution passes from a reddish-yellow to a clear green if all the chromic acid is reduced; if not, the solution has a dark greenish-brown colour.

As examples of substances which are oxidised by chromic acid or by potassium dichromate (or chromate) in presence of sulphuric acid, sulphurous acid, hydrochloric acid, hydrogen sulphide, and ferrous sulphate may be taken.

In the first case the final results are expressed by the equation,*

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O,$$

and the intermediate stages may be represented as follows,

$$K_2Cr_2O_7 + H_2SO_4 + H_2O = K_2SO_4 + 2H_2CrO_4$$
$$2H_2CrO_4 + H_2O = 3O + 2Cr(OH)_3$$
$$3H_2SO_3 + 3O = 3H_2SO_4 \; *$$
$$2Cr(OH)_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 6H_2O.$$

Hence *one molecule* of potassium dichromate gives *three atoms* of oxygen, which are available for the oxidation of the reducing agent; as, in presence of sulphuric acid, two molecules of a chromate give one molecule of a dichromate (see p. 504), *two molecules* of potassium chromate also yield *three atoms* of available oxygen.

In the oxidation of hydrochloric acid, the reaction only takes place readily on heating the substances together in concentrated solution, and is expressed by the equation,

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O.$$

The chlorine which is liberated is equivalent to the available oxygen, and chromium chloride is formed by the interaction of the acid and the basic hydroxide, $Cr(OH)_3$.

Chlorine may be prepared by heating concentrated hydrochloric acid with coarsely powdered potassium dichromate, which also oxidises hydrobromic and hydriodic acids very readily.†

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* It should be observed that in the above reaction three out of the four molecules of sulphuric acid which are required for the formation of the metallic sulphates are *formed* by the oxidation of the sulphurous acid

† Pure potassium dichromate is often used in standardising solutions of sodium thiosulphate (p. 496). When it is added to a solution containing excess of potassium iodide and sulphuric acid, it oxidises the hydrogen iodide in the solution, and the latter may then be titrated with sodium thiosulphate. The quantity of iodine which has been liberated by the known weight of dichromate ($K_2Cr_2O_7 = 3I_2$) being known, the strength of the thiosulphate solution may be calculated.

When hydrogen sulphide is passed through an acidified solution of potassium dichromate (as is sometimes done in qualitative analysis) the solution ultimately turns green, and sulphur separates as a fine, pale-yellow powder,*

$$K_2Cr_2O_7 + 8HCl + 3SH_2 = 2KCl + 2CrCl_3 + 3S + 7H_2O.$$

The action of ferrous sulphate on an acidified solution of potassium dichromate is expressed thus,

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O,$$

because, as already shown (p. 453), one atom of oxygen oxidises two molecules of ferrous sulphate.†

Potassium dichromate is decomposed when it is strongly heated with concentrated sulphuric acid; the chromic anhydride which is first produced undergoes the decomposition mentioned above, and the chromium sesquioxide is then converted into sulphate,

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3O_2 + 8H_2O$$

This reaction is sometimes used for the preparation of oxygen. Potassium dichromate also gives oxygen, together with potassium chromate and chromium sesquioxide, when it is heated alone,

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$

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* The separation of this precipitate by filtration generally gives trouble; for this reason, when a chromate or dichromate is known to be present in the mixture to be analysed, sulphurous acid is added to the acid solution until the colour changes to green (or reduction is complete), and the solution is then boiled until free from sulphurous acid. If the addition of sulphurous acid produces a precipitate, owing to the formation of some insoluble sulphate, the dichromate is reduced with hydrochloric acid instead.

† The quantity of a ferrous salt in a solution may be determined by titration with a standard solution of potassium dichromate instead of potassium permanganate (p. 453), and this process is used when the solution contains chlorides, because dilute hydrochloric acid reduces permanganates but does not reduce dichromates. A special indicator (potassium ferricyanide, p. 705) is required in this titration.

Potassium dichromate (or sodium dichromate) is used as an oxidising agent in the colour industry ; it is also employed in dyeing, in electric batteries, in preparing other chromium compounds, and in making carbon prints.

The only other dichromates of any importance are sodium dichromate, a red, crystalline, readily soluble, hygroscopic salt, and ammonium dichromate (p. 516).

Chromyl chloride, CrO_2Cl_2, distils and condenses to a dark-red liquid (very like bromine) when a mixture of potassium dichromate and a *chloride* is heated with concentrated sulphuric acid,

$$CrO_3 + 2HCl = CrO_2Cl_2 + H_2O.$$

It is decomposed by water, giving hydrochloric and chromic acids, and is therefore an acid chloride, corresponding with sulphuryl chloride (p. 492).

Bromides and iodides treated in the above manner do not give rise to volatile chromyl compounds, and the free halogens, produced by the oxidation of the halogen acids, distil over. Hence a chloride may be detected in presence of a bromide or an iodide, or both, by distilling the mixture with dichromate and sulphuric acid, boiling the distillate with water to decompose the chromyl chloride and to expel the free halogens, and then testing the remaining solution for *chromic acid.*

CHROMATES.

Chromates are obtained from chrome iron ore as already described ; also when chromium sesquioxide (p. 511) is fused with an alkali hydroxide or alkali carbonate and some oxidising agent such as potassium nitrate or chlorate ; also when this oxide is heated with sodium peroxide (p. 671),

$$Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O,$$

or when an aqueous solution of a chromium salt, such as chromic sulphate, is treated with sodium peroxide. In the last case the salt is decomposed by the sodium hydroxide, which is formed from the peroxide, and the chromic hydroxide thus produced is then oxidised.

Chromates are also formed when dichromates are treated with basic hydroxides, the *red* colour of the dichromate giving place to the *yellow* colour of the chromate,

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Insoluble chromates are also formed when a solution of a *di*chromate (or, of course, of a soluble chromate) is treated with solutions of certain metallic salts; thus on a solution of barium chloride being added to a solution of potassium dichromate, barium chromate (and not the dichromate) is precipitated,

$$K_2Cr_2O_7 + 2BaCl_2 + H_2O = 2BaCrO_4 + 2KCl + 2HCl.$$

Potassium chromate, K_2CrO_4, is a lemon-yellow, crystalline, anhydrous salt, readily soluble in water; it melts at a high temperature, but does not decompose. As it is converted into dichromate by acids, it gives in acid solution the reactions of the dichromate; in neutral solution, potassium chromate is reduced by hydrogen sulphide,

$$2K_2CrO_4 + 3H_2S + 2H_2O = 4KOH + 2Cr(OH)_3 + 3S.$$

Silver chromate, Ag_2CrO_4, is obtained as a dark-red precipitate when an aqueous solution of a chromate or of a dichromate (see above) is treated with a solution of silver nitrate; it dissolves chemically in nitric acid, giving silver nitrate and chromic acid.

Barium chromate, $BaCrO_4$, prepared by precipitation (see above), is a pale-yellow solid, insoluble in water and in acetic acid, but it dissolves chemically in hydrochloric acid.

Lead chromate, $PbCrO_4$, occurs in nature as a yellow mineral (*crocoisite*), and is obtained as a pale-yellow precipitate on solutions of potassium chromate and lead acetate being mixed (p. 279). It is insoluble in water, and is used as a paint (*chrome yellow*). It melts at high temperatures without decomposing, but in presence of reducing agents, such as carbon compounds, it acts as an oxidising agent at high temperatures, and is converted into lead oxide and *lead chromite*, $Pb(CrO_2)_2$ or PbO, Cr_2O_3, with loss of oxygen

CHROMIUM SALTS.

The green solution obtained by the reduction of potassium dichromate with sulphurous acid in presence of sulphuric acid contains molecular proportions of potassium sulphate and chromium sulphate (p. 506), and when concentrated and left for some time, it deposits dark bluish-violet octahedral crystals of chrome alum, $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$; this double salt (p. 322) dissolves in water, giving a violet solution which turns green when it is boiled owing to the occurrence of hydrolysis, and the consequent production of green basic salts.

Basic Salts. — When the normal salt derived from a dihydric or polyhydric basic hydroxide (that is to say, from a basic hydroxide which contains two or more hydroxyl-groups in its molecule) undergoes hydrolysis, one or more of the acid radicles may be displaced by hydroxyl-groups. The products thus formed are called *basic salts* so long as they still contain one or more acid radicles Thus the compounds $BiCl(OH)_2$ and $BiOCl$, which are formed by the hydrolysis of normal bismuth chloride (p. 361), are basic salts, and a compound such as $Cr_2(SO_4)_2(OH)_2$, formed by the hydrolysis of normal chromic sulphate,

$$Cr_2(SO_4)_3 + 2H_2O \leftarrow \rightarrow Cr_2(SO_4)_2(OH)_2 + H_2SO_4,$$

would also be a basic salt.

The composition of a basic salt depends very much on the conditions under which it has been prepared, because the extent of the hydrolysis of a normal salt, like all reversible reactions, depends on the relative concentrations of the reacting substances. For this reason many basic salts are probably mixtures, and the formulæ given to them may be regarded as expressing their compositions only approximately. In many cases the composition of a basic salt is represented by a formula such as $CuCO_3$, $Cu(OH)_2$, or $2PbCO_3$, $Pb(OH)_2$; such formulæ do not necessarily imply that the salts are mere mixtures of normal salt and basic hydroxide, but are used because the precise nature of the basic salt is not known.

As the formation of a basic salt is a reversible reaction, when a basic salt is treated with a concentrated solution of an acid it gives a normal salt and water, and thus shows the behaviour of a basic hydroxide as well as that of a salt.

Chromic hydroxide, $Cr(OH)_3$, is obtained in a *hydrated* form, as a pale-blue precipitate, when an alkali hydroxide is added to the above solution of chrome alum, or to a solution of any chromic salt,

$$Cr_2(SO_4)_3 + 6NH_4(OH) = 2Cr(OH)_3 + 3(NH_4)_2SO_4.$$

It is insoluble in water, but it is essentially a basic hydroxide and dissolves chemically in acids, forming chromic salts.

It acts, however, as an acid towards many basic hydroxides, thus with potassium or sodium hydroxide it forms soluble chromites, which, like chrome iron stone, may be regarded as derivatives of *chromous acid*, $HCrO_2$. The soluble chromites are hydrolysed when their solutions are boiled and a greenish precipitate of chromic hydroxide is formed.

Chromium sesquioxide, Cr_2O_3,* is formed when (carefully washed) chromic hydroxide is heated gently, and also when chromic anhydride is heated (p. 505). Although a basic oxide, it is insoluble in acids.

A hydrated variety of chromium sesquioxide, obtained by heating a mixture of potassium dichromate and boric acid (p. 607), and then extracting the soluble matter with water, is used as a pigment under the name of *Guignet's green*.

The chromic salts, such as chromic sulphate, correspond with the oxide Cr_2O_3 and the hydroxide $Cr(OH)_3$. **Chromic sulphate,** $Cr_2(SO_4)_3$, prepared by dissolving the *hydroxide* in sulphuric acid, forms reddish violet crystals and is soluble in water, giving a violet solution, which turns green when it is heated (p. 510).

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* As the name 'chromic trioxide,' given sometimes to CrO_3, is rather ambiguous, it is better to keep to the names used above.

Chromic chloride, $CrCl_3$, is probably formed when the hydroxide is dissolved in concentrated hydrochloric acid, but on the solution being evaporated on a water-bath a basic salt, or even chromic hydroxide, remains, owing to the occurrence of hydrolysis. Anhydrous chromic chloride volatilises when an intimate mixture of chromium sesquioxide and carbon is very strongly heated in a stream of chlorine in a porcelain tube,

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

The product condenses on the cooler portions of the tube in beautiful peach-coloured crystals, which dissolve very slowly in boiling water, giving a green solution. This method of decomposing an oxide by the *combined* action of carbon and chlorine is employed in the preparation of several other chlorides (p. 580); neither chlorine nor carbon *alone* acts on the oxide at the temperature used in this experiment (p. 340).

Chromous Compounds.—Chromium dissolves chemically in hot hydrochloric acid, hydrogen is rapidly evolved, and a green solution of chromic chloride is obtained; when this solution is treated with zinc it turns blue, owing to the reduction of the chromic salt to **chromous chloride,** $CrCl_2$.

A yellow **chromous hydroxide,** $Cr(OH)_2$, is also known.

Chromium, like sulphur, is sexvalent in its highest salt-forming oxide, (CrO_3), and the acids derived from this anhydride are of the same type and of the same *structure* as the corresponding derivatives of sulphur; for this reason the structural formulæ of the chromates and dichromates have not been given. Except that the chromates are isomorphous with the corresponding sulphates (in consequence of their similarity in type), there is little in common between the two classes of compounds, and the relationship between the metal chromium and the non-metal sulphur is a very slight one. The relationship, in fact, is comparable to that between manganese and the halogens (p. 455), the position of chromium in the periodic system being altogether different from that of the oxygen sub-family; in harmony with its position, chromium forms a connecting link between vanadium and manganese.

Molybdenum (Mo), tungsten or wolfram (W), and uranium (U) are three elements related to chromium. **Molybdenum** occurs in nature as *molybdenite*, MoS_2, and when this sulphide is heated in the air it gives **molybdic anhydride,** MoO_3. **Ammonium molybdate,** $(NH_4)_2MoO_4$, is prepared by treating the anhydride with ammonium hydroxide; its solution gives with nitric acid a crystalline precipitate of molybdic acid, which dissolves again on excess of diluted nitric acid being added. This solution, 'ammonium nitromolybdate,' is used as a reagent for phosphoric and arsenic acids (pp. 550, 558).

Tungsten occurs as **ferrous tungstate,** $FeWO_4$, from which **sodium tungstate** may be prepared by heating with sodium carbonate and then extracting the product with water. This salt is used as a mordant, and also for impregnating fabrics in order to render them less readily inflammable and combustible. Tungsten is sometimes added to steel, which it renders very hard; tungsten filaments are used in electric lamps.

Uranium occurs in *pitchblende*: its compounds are used in making a yellowish-green fluorescent glass (uranium glass), and **uranyl acetate** is employed for the volumetric estimation of phosphoric acid. Uranium forms compounds in which its valency varies from four (UCl_4) to eight (UO_4), and is also interesting as being the element of highest atomic weight; the *uranyl* salts are derived from the *hydroxide* $UO_2(OH)_2$.

CHAPTER LI.

The Nitrogen Family

NITROGEN, N_2; AT WT. 14·0.

Nitrogen, so named from its occurrence in nitre, is one of the members of a family of elements which also includes phosphorus, arsenic, antimony, and bismuth.

Although under most conditions nitrogen is very inert, and for this reason occurs in nature in the free state, it forms very many compounds, some of which, namely, the *albuminoids* and *proteins*, are essential components of animals and plants. These substances, as, for example, egg albumin (white-of-egg) and gluten (wheat albumin), contain carbon, nitrogen, oxygen, hydrogen, and sulphur. Such substances, and many other materials of a related character, are often referred to as 'nitrogenous organic matter.'

In addition to these highly complex substances or mixtures, many relatively simple compounds of nitrogen are known, as, for example, those which it forms with hydrogen, with oxygen, and with both these elements. The most important naturally occurring mineral compounds of nitrogen are the nitrates of potassium and sodium (p. 241).

As already stated (p. 93), the 'atmospheric nitrogen' which remains when carbon dioxide and oxygen have been removed from dry air is not pure nitrogen, but for practical purposes the presence of argon and the other inert gases (p. 681) is of no importance; consequently in most experiments atmospheric nitrogen is employed instead of the pure gas.

In addition to the methods already given for its preparation (pp. 90–92), nitrogen may be obtained by bubbling air through a concentrated solution of ammonium hydroxide, and then passing the mixture of air and ammonia through a tube containing heated copper. The atmospheric oxygen is fixed by the copper, and the copper oxide thus formed oxidises the ammonia (p. 263), with formation of nitrogen, water, and copper. Hence, if excess of ammonia is used, the copper remains unchanged, and the process may be continued indefinitely. The escaping gas is bubbled through dilute sulphuric acid to free it from ammonia, and the nitrogen, which is *partly* 'atmospheric,' may then be collected in a gas-holder.

Another method consists in burning a jet of hydrogen in a slow stream of air (fig. 10, p. 105), whereby most of the oxygen is removed, and then passing the atmospheric nitrogen over heated copper to free it completely from oxygen. Another method is to suspend a bag of moistened iron filings in a large bottle (*a*) forming part of the apparatus shown in fig. 101 (p. 517). As the oxygen in the air contained in the bottle (*a*) is absorbed, water flows in from the reservoir (*b*). When all the oxygen has been removed, the nitrogen may be driven out by raising the reservoir (*b*) and opening a pinch-tap which ordinarily closes the tube (*c*).

Nitrogen free from atmospheric gases may be prepared from nitric acid (p. 238), from oxides of nitrogen (pp. 244, 269), and from ammonia (p. 263); also, and more conveniently, by cautiously heating a solution of *ammonium nitrite*, a reaction which is comparable with that which occurs when nitrous oxide is prepared from ammonium nitrate (p. 270),

$$NH_4NO_2 = N_2 + 2H_2O.$$

As ammonium nitrite is not easily prepared, ammonium sulphate is added to a concentrated aqueous solution of sodium nitrite (p. 527), and the mixture is gently heated. The reversible reaction;

$$2NaNO_2 + (NH_4)_2SO_4 \longleftrightarrow 2NH_4NO_2 + Na_2SO_4,$$

then takes place, but as the ammonium nitrite decomposes the change proceeds continuously from left to right.

In order to obtain pure nitrogen, the gas prepared by this or other methods may be passed over strongly heated copper or iron in order to free it from oxides of nitrogen which may be present. The gas may then be dried with sulphuric acid or phosphorus pentoxide.

Nitrogen is also obtained, but in an impure condition, when a mixture of potassium dichromate and ammonium chloride is heated; the *ammonium dichromate* which is thus formed readily decomposes,

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

Nitrogen is also formed when a solution of bleaching powder is cautiously added to a boiling solution of *excess* of ammonium sulphate.*

Nitrogen melts at −214°, and boils at −195°. When liquid air boils, the more volatile nitrogen passes away first, then the oxygen, and lastly the denser inert gases of the atmosphere.

Nitrogen is not very easily identified or detected, but this may be done, after the other gases present are absorbed, by 'sparking' the sample with some oxygen in a eudiometer (p. 247), or by heating magnesium in the sample and then testing the product as described later (p. 517).

Nitrogen combines directly with hydrogen when the two gases are 'sparked' together. The decomposition of ammonia already studied (p. 264) is a reversible reaction, and equilibrium is reached when 98 per cent. of the ammonia is decomposed; but if a mixture of hydrogen (3 vols.) and nitrogen (1 vol.) is confined in a eudiometer over dilute sulphuric acid and sparked, the ammonia which is produced is absorbed, and consequently the reaction proceeds slowly but continuously from left to right,

$$3H_2 + N_2 \longleftrightarrow 2NH_3.$$

This is a very good illustration of the effect of concentration on the direction of a reversible reaction (p. 353).

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* Unless care is taken to keep the ammonium sulphate in large excess, explosions may occur owing to the formation of nitrogen trichloride (p. 521).

Nitrogen combines directly not only with oxygen and with hydrogen but also with many other elements at very high temperatures. Some of the compounds thus formed are termed *nitrides*.

Magnesium nitride, Mg_3N_2, is produced when the metal is heated in nitrogen at a temperature above 800°; the nitride is decomposed by boiling water, giving ammonia and magnesium hydroxide,

$$Mg_3N_2 + 6H_2O = 2NH_3 + 3Mg(OH)_2,$$

so that the formation of the nitride is easily demonstrated.

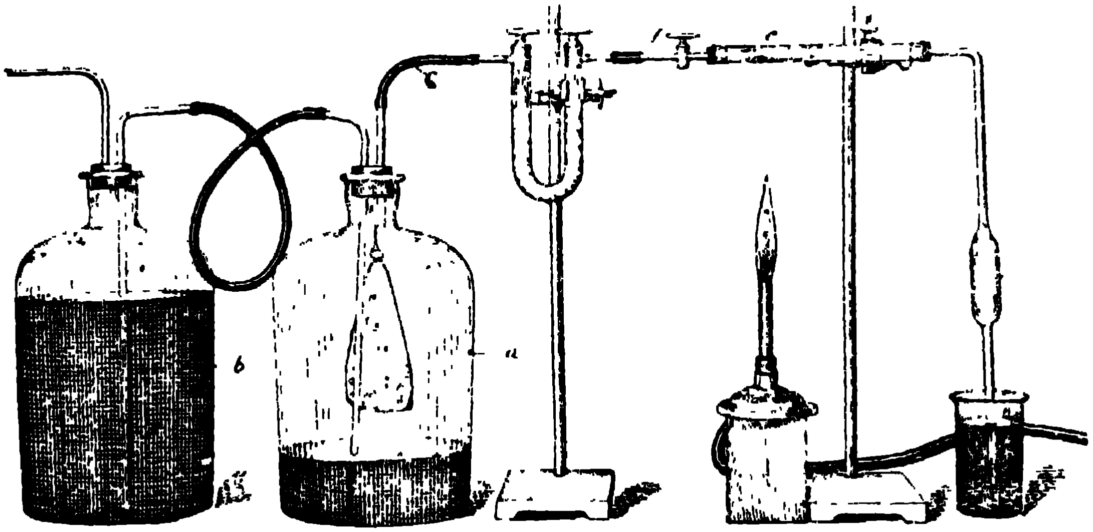

Fig. 104.

In order to show the combination of nitrogen and magnesium, the dry gas is passed through the hard-glass tube (*e*, fig. 104), which contains a little powdered magnesium, until all the air is expelled. The tap (*f*) is then closed, and the magnesium is heated, first with a Bunsen-flame and then with an oxy-coal-gas blowpipe flame (p. 135). The escape of nitrogen from the pipette (owing to the expansion of the gas) soon ceases, and when the magnesium has reached a sufficiently high temperature the water begins to rise in the pipette, owing to the absorption of the gas by the magnesium.

Nitrogen also combines with calcium to form **calcium**

nitride, Ca_3N_2, with aluminium to form **aluminium nitride,** AlN, and with other metals.

The Utilisation of Atmospheric Nitrogen.—Although so large a proportion of the atmosphere consists of nitrogen, this gas is not directly absorbed by plants, and the whole of the nitrogen essential to vegetable growth is taken up in a combined form through the roots of the plant. Some leguminous plants (peas, beans, clover, &c.) are provided **with root 'nodules,' which contain certain 'nitrogen-fixing' bacteria capable of absorbing *atmospheric* nitrogen and converting** it into nitrogenous compounds, such plants, therefore, need no nitrogenous manures; but others, when grown many years in succession on the same ground, gradually exhaust the soil, which must then be supplied with nitrates or ammonium salts if good crops are to be obtained. One method of avoiding the necessity for the direct application of nitrogenous **manures is to 'sow' the ground with preparations of the 'nitrogen-fixing' bacteria* obtained from leguminous plants, but hitherto the use of sodium nitrate or ammonium sulphate (p. 267) has given better results.**

Now the quantities of these substances which are available are not very large, and consequently many attempts have been made to prepare nitrates and ammonium salts from atmospheric nitrogen. The production of *nitrates* from atmospheric nitrogen has already been referred to (p. 299), and the methods for the preparation of *ammonium salts* may now be briefly described.

When nitrogen is passed over a mixture of carbon and potassium hydroxide which is at a white heat, a salt, potassium cyanide (p. 679), is formed, and when this compound is warmed with dilute sulphuric acid it gives ammonium sulphate. These reactions, however, cannot be satisfactorily carried out on the large scale.

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* The term 'nitrifying' bacteria is not applied to those organisms which are capable of fixing atmospheric nitrogen, but only to those which bring about the formation of nitrates from nitrogenous organic matter (p. 241).

When commercial calcium carbide, CaC_2 (p. 638), is heated under pressure in an atmosphere of pure nitrogen,* the gas is absorbed and **calcium cyanamide** is formed,

$$CaC_2 + N_2 = CaN{\cdot}CN + C.$$

The product, a mixture of calcium cyanamide and carbon, is known commercially as *Nitrolim* or *Kalkstickstoff;* when treated with water it slowly undergoes decomposition, giving finally calcium carbonate and ammonia,

$$CaN{\cdot}CN + 3H_2O = CaCO_3 + 2NH_3.$$

Nitrolim may be used directly as a manure, for which purpose it is applied before sowing or planting is done, or it may be first employed for the preparation of ammonium sulphate.

Nitrolim is also used for the manufacture of cyanides.

COMPOUNDS OF NITROGEN AND HYDROGEN.

Ammonia (p. 260) is formed in small quantities during the destructive distillation of horn, bone, cheese, gluten, and other nitrogenous organic matter (hence its presence in gas-liquor, p. 267); also, when such substances are heated with soda lime. In the latter case most of the combined nitrogen in the material is converted into ammonia. It is also formed in small quantities during the putrefaction or decay of nitrogenous organic matter, also by the reduction of nitric acid (p. 530) and other nitrogen compounds.

Liquid ammonia boils at $-34°$. As the gas is easily liquefied by pressure alone, and the evaporation of the liquid is attended by absorption of heat, liquid ammonia is often used for refrigerating purposes.

Minute traces of ammonia, or of ammonium salts, in aqueous solution—as, for example, in natural waters contaminated with sewage—may be detected with the aid of Nessler's solution

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* The pure nitrogen required for this purpose may be obtained by liquefying air which has been freed from moisture and carbon dioxide, and then separating the oxygen and nitrogen by fractional distillation (p. 684).

(p. 633), which gives a distinct yellow colouration with a solution containing only 1 part of ammonia in 5,000,000 of water.

The more important ammonium salts have been described (pp. 264–268), and it has been pointed out that all such salts may be regarded as derived from ammonium hydroxide, $NH_4{\cdot}OH$ (p. 266).* A compound of this composition has recently been obtained in the solid state, but it is stable only at very low temperatures.

It is a very interesting fact that the univalent basic radicle, *ammonium* (p. 266), may play the part of a single atom of sodium (or of one of the other univalent metals). Not only does this radicle take the place of hydrogen in acids, forming ammonium salts, but these salts are often isomorphous with those of sodium, &c.; that is to say, the substitution of the radicle NH_4- for the single atom $Na-$, $K-$, $Ag-$ in a molecule may not change the structure of the crystals formed from these molecules. Potash alum and ammonium alum (or ammonia alum), for example, are isomorphous double salts (p. 295). The close relationship between certain ammonium salts and corresponding potassium salts is further illustrated in the case of the platinichlorides and acid tartrates of ammonium and potassium (p. 678).

In some respects, of course, ammonium salts differ widely from sodium salts. The former either sublime or lose ammonia and water (p. 549) when they are strongly heated. They are also completely decomposed when they are heated not only with sodium hydroxide, but with other basic hydroxides or basic oxides; † this is due to the fact that ammonium hydroxide readily decomposes, giving volatile products (ammonia and water), in consequence of which reactions such as,

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* The formula $NH_4{\cdot}OH$ or NH_4 OH is often used instead of $NH_4(OH)$; all these formulæ are intended to indicate that the molecule contains a hydroxyl-group, which, like the four hydrogen atoms, is directly united to the atom of nitrogen.

† This fact may be utilised in qualitative analysis in testing whether a given substance is a basic hydroxide or basic oxide; for this purpose the substance is heated with solid ammonium chloride.

$$(NH_4)_2SO_4 + 2NaOH \longleftrightarrow Na_2SO_4 + 2NH_4{\cdot}OH,$$

which are reversible in aqueous solution, proceed continuously from left to right when the solution is boiled, or in absence of any appreciable quantity of water.

Sodamide, NH_2Na, is obtained as a colourless solid when dry ammonia is passed over sodium which is heated at about 350°; it is decomposed by water, giving ammonia and sodium hydroxide.

Nitrogen chloride, NCl_3, separates as a heavy oil when chlorine is passed into a concentrated aqueous solution of ammonium chloride. It is a most dangerous explosive.

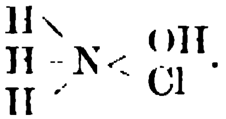
A solution of nitrogen chloride in carbon tetrachloride is fairly stable, and may be obtained by carrying out the above reaction in presence of the tetrachloride. The molecular formula of nitrogen chloride is not known; it may be $Cl_3N:NCl_3$.

Nitrogen iodide, $H_3N:NI_3$, is obtained as a black powder when an alcoholic solution of iodine is added to a solution of ammonium hydroxide. The *dry* substance is extremely explosive, and detonates violently even when rubbed with a feather; it also explodes violently when it is placed in boiling water.

HYDROXYLAMINE, NH_2-OH.

This compound, so named because it consists of a hydroxyl-group united to an *amino*-group, $-NH_2$, may be regarded as derived from ammonia by the substitution of the univalent $-OH$ group for an atom of hydrogen. Its aqueous solutions give with acids *hydroxylamine salts*, such as the *hydrochloride* $NH_2{\cdot}OH, HCl$, and the *sulphate* $(NH_2{\cdot}OH)_2, H_2SO_4$, so that hydroxylamine is a base in aqueous solution. From the compositions of these salts it will be seen that the molecules of hydroxylamine and of acid unite directly, and this idea is expressed in the above formulæ.

These formulæ, however, although generally used, are unsatisfactory, inasmuch as they do not bring out what is probably the fact—namely, that the nitrogen atom, which is tervalent in hydroxylamine, is quinquevalent in the hydroxylamine salts, as it is in the ammonium salts; hydroxylamine hydrochloride, for example, has probably the structure,



$$\begin{matrix} H \diagdown & & \\ H - & N < & \begin{matrix} OH \\ Cl \end{matrix} . \\ H \diagup & & \end{matrix}$$

It may be that hydroxylamine, like ammonia, combines with water to form a hydroxide, $HO{\cdot}NH_3{\cdot}OH$, which then interacts with acids just as do other basic hydroxides,

$$HO{\cdot}NH_3{\cdot}OH + HCl = HO{\cdot}NH_3Cl \text{ (or } NH_2{\cdot}OH, HCl) + H_2O.$$

Hydroxylamine is formed when hydrochloric acid, mixed with a little dilute nitric acid, is left in contact with tin, or when nitric oxide is passed through hydrochloric acid which is reacting with tin; in both these cases the nascent hydrogen (p. 311) produced from the metal and the hydrochloric acid reduces the nitrogen compound,

$$HNO_3 + 6H = NH_2{\cdot}OH + 2H_2O,$$
$$2NO + 6H = 2NH_2{\cdot}OH,$$

and the hydroxylamine thus formed combines with some of the hydrochloric acid to form hydroxylamine hydrochloride, $NH_2{\cdot}OH, HCl$.

In this operation ammonia is also formed by a further reduction process,

$$NH_2{\cdot}OH + 2H = NH_3 + H_2O,$$

so that the solution also contains ammonium chloride. After hydrogen sulphide is passed through the solution, and the solution is filtered from the precipitated stannous sulphide,

$$SnCl_2 + SH_2 = SnS + 2HCl,$$

the liquid is evaporated to dryness, and the residue is extracted with alcohol, in which hydroxylamine hydrochloride is soluble, ammonium chloride insoluble.

Hydroxylamine is best prepared, in the form of its sulphate, by passing sulphur dioxide into a well-cooled concentrated solution of sodium nitrite (2 gram-molecules) and sodium carbonate (1 gram-molecule) until the solution acquires an acid reaction. The solution, which contains **sodium hydroxylamine disulphonate,**

$$HO{\cdot}NO + 2NaHSO_3 = HO{\cdot}N(SO_3Na)_2 + H_2O,$$

is then treated with a few drops of sulphuric acid, and is kept at about 90° during forty-eight hours. The disulphonate is thus hydrolysed with formation of hydroxylamine and sodium hydrogen sulphate,

$$HO{\cdot}N(SO_3Na)_2 + 2H_2O = NH_2{\cdot}OH + 2NaHSO_4,$$

which interact to form hydroxylamine sulphate and sodium sulphate,

$$2NH_2{\cdot}OH + 2NaHSO_4 = (NH_2{\cdot}OH)_2, H_2SO_4 + Na_2SO_4.$$

On the solution being evaporated, after neutralising with sodium carbonate, sodium sulphate is deposited first, and the crystals of hydroxylamine sulphate, obtained from the mother-liquor, are purified by recrystallisation from water.

An aqueous solution of hydroxylamine is obtained when a solution of the hydrochloride (or sulphate) is treated with sodium hydroxide, and such a solution (which also contains a sodium salt) is generally used instead of a solution of the pure base. Such a solution gives nitrogen and ammonia when it is boiled,

$$3NH_2{\cdot}OH = N_2 + NH_3 + 3H_2O,$$

and reduces solutions of copper salts (Fehling's solution); giving finally a precipitate of cuprous oxide with liberation of nitrous oxide,

$$2NH_2{\cdot}OH + 4CuO = 2Cu_2O + N_2O + 3H_2O.$$

Pure anhydrous hydroxylamine may be prepared by treating hydroxylamine hydrochloride with normal sodium phosphate in concentrated aqueous solution; the sparingly soluble hydroxylamine phosphate which crystallises out is dried and then heated under greatly reduced pressure. The distillate, which consists of the impure base,

$$(NH_2{\cdot}OH)_3, H_3PO_4 = 3NH_2{\cdot}OH + H_3PO_4 \text{ (residue)},$$

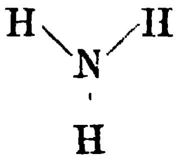
is purified by recrystallisation from alcohol at low temperatures.

Hydroxylamine melts at 33°, and decomposes or explodes when heated under atmospheric pressure; it is readily soluble in water, giving a strongly alkaline solution.

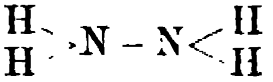
It is a monacid base, and forms normal salts such as the *hydrochloride* $NH_2{\cdot}OH, HCl$, and *sulphate* $(NH_2{\cdot}OH)_2, H_2SO_4$, which are crystalline and readily soluble in water.* Hydroxylamine is used as a reducing agent and in the study of organic (carbon) compounds.

HYDRAZINE AND AZOIMIDE.

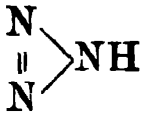
Two simple compounds of nitrogen and hydrogen are known in addition to ammonia—namely, hydrazine and azoimide or hydrazoic acid. In these compounds, as in ammonia, the element nitrogen seems to be tervalent, as indicated in the following formulæ,



Ammonia



Hydrazine



Azoimide

and yet only two of the three substances are related to one another in properties.

Hydrazine, like ammonia (and like hydroxylamine), gives aqueous solutions which have an alkaline reaction and which yield salts with acids. These salts may be regarded as having been formed from the hydroxide (hydrazonium hydroxide),

$$\begin{array}{l} NH_3{\cdot}OH \\ | \\ NH_3{\cdot}OH \end{array} + 2HCl = \begin{array}{l} NH_3Cl \\ | \\ NH_3Cl \end{array} + 2H_2O,$$

just as ammonium chloride is formed from ammonium hydroxide, although their compositions are generally expressed by formulæ such as $N_2H_4, 2HCl$, or $NH_2{\cdot}NH_2, 2HCl$

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* It should be noted that salts obtained by the combination of hydroxylamine and other derivatives of ammonia with the halogen acids are called *hydro*chlorides, *hydro*bromides, &c., whereas salts with other acids are named in the usual manner.

for a reason similar to that given in the case of the hydroxylamine salts (p. 521). In the hydrazine salts, therefore, the element nitrogen is quinquevalent.

Azoimide or *hydrazoic acid*, as its name implies, is a compound of very different properties, and the hydrogen atom which it contains is displaceable by metals; it shows the general behaviour of an acid.

Hydrazine may be regarded as a simple derivative of ammonia; as ammonia in which an atom of hydrogen has been displaced by the univalent group $-NH_2$. In accordance with this view, these two compounds are similar in their general chemical behaviour. Thus they both combine with water forming basic hydroxides, but whereas ammonium hydroxide is extremely unstable (p. 520), **hydrazonium hydroxide** (hydrazine hydrate), $NH_2{\cdot}NH_3{\cdot}OH$, may be isolated, and possibly the dihydroxide, $HO{\cdot}NH_3{\cdot}NH_3{\cdot}OH$, exists in aqueous solution.

The salts which hydrazoic acid forms with ammonia and with hydrazine respectively have the compositions $N_3{\cdot}NH_4$ and N_3H, N_2H_4 respectively, so that altogether five compounds of hydrogen and nitrogen are known.

Hydrazine, NH_2-NH_2, is easily prepared by adding a solution of sodium hypochlorite to excess of a concentrated solution of ammonium hydroxide, which contains about 2 parts per 10,000 of ordinary joiner's glue.* The solution is boiled to expel unchanged ammonia, and, after having been concentrated, is mixed with sulphuric acid, whereon hydrazine sulphate, N_2H_4, H_2SO_4, separates in crystals.

When this salt is distilled with very concentrated potassium hydroxide solution under reduced pressure, a solution of hydrazonium hydroxide (hydrazine hydrate) is obtained, and the hydroxide or hydrate, N_2H_4, H_2O, may then be isolated by fractional distillation as a colourless liquid which distils and dissociates at about 119°. Hydrazine may be prepared by distilling this hydroxide with barium oxide under reduced pressure.

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* In absence of glue very little hydrazine is obtained, but the action of the glue is not understood.

Hydrazine is a colourless fuming liquid, boiling at 114°. It combines with water to form the hydroxide, which acts either as a monacid or as a diacid base (p. 256).

Hydrazine is a very vigorous reducing agent. It precipitates cuprous oxide from Fehling's solution (p. 656), and reduces ammoniacal silver hydroxide (p. 661) to silver, being itself oxidised to nitrogen; it is poisonous.

Azoimide or **hydrazoic acid,** N_3H, is obtained in the form of its sodium salt when nitrous oxide is passed over sodamide (p. 521) which is heated at about 200°,

$$N_2O + NH_2Na = N_3Na + H_2O.$$

The free acid may be obtained in aqueous solution by distilling the sodium salt with dilute sulphuric acid.*

The solution is acid to litmus, acts on certain metals giving hydrogen, and with silver nitrate it yields insoluble **silver azoimide,** N_3Ag. This and some other salts, as well as the anhydrous acid (a liquid boiling at 37°), are *extremely explosive*.

THE OXY-ACIDS OF NITROGEN.

NITROUS ACID, HNO_2 OR $O=N-O-H$, AND ITS DERIVATIVES.

It has already been stated (p. 242) that the nitrates of sodium and potassium differ from most metallic nitrates in their behaviour at high temperatures, inasmuch as they are converted into the corresponding *nitrites* when they are very strongly heated,

$$2KNO_3 = 2KNO_2 + O_2.$$

In presence of lead, this decomposition takes place at lower temperatures (about 500°), and in preparing sodium nitrite

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* Also by treating hydrazine with nitrous acid in aqueous solution,

$$N_2H_4 + HNO_2 = N_3H + 2H_2O.$$

commercially, lead is added to the fused nitrate (Chili saltpetre),

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

The product is run into water, the solution (which contains sodium hydroxide in small quantities) is neutralised with nitric acid, and after the insoluble lead oxide is separated, the liquid is evaporated and then allowed to crystallise. Potassium nitrite is prepared from nitre in a similar manner.

Sodium nitrite, $NaNO_2$, and **potassium nitrite**, KNO_2, are readily soluble in water. When an acid (hydrochloric, sulphuric, acetic, &c.) is added to their solutions, **nitrous acid** is liberated; but if the solution is not very dilute most of the acid immediately decomposes into its *anhydride* and water,

$$2HNO_2 = N_2O_3 + H_2O,$$

and a brown gas is evolved (see below). Nitrous acid, like carbonic acid, exists only in *cold* dilute aqueous solution, and such a solution has a pale-blue colour. It liberates iodine from potassium iodide (p. 416),

$$KI + HNO_2 = KNO_2 + HI$$
$$2HI + 2HNO_2 = 2NO + I_2 + 2H_2O\ ;$$

and in this reaction acts as an oxidising agent, being itself reduced to nitric oxide. Towards potassium permanganate, however, it acts as a reducing agent, and is converted into nitric acid,

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

Nitrites are easily detected by their behaviour towards dilute acids.

Large quantities of nitrites are used in the colour industry, and nitrous acid is a very important reagent in the study of carbon compounds.

Nitrous anhydride, N_2O_3, one of the five oxides of nitrogen (p. 270), is not a very stable compound at ordinary temperatures. It is obtained as a green liquid when sodium or potassium nitrite is treated with dilute sulphuric acid, and the evolved gas, dried with the aid of calcium chloride, is led into a vessel immersed in a freezing mixture of ice and salt (footnote, p. 8).

A similar product is obtained when arsenious anhydride (p. 555) is very gently warmed with concentrated nitric acid, and the evolved gas is treated in the manner just described; in this reaction the nitric acid is reduced to nitrous acid, and the arsenious anhydride is oxidised to arsenic acid (p. 558).

Nitrous anhydride dissociates very readily, and at ordinary temperatures it is converted into a dark-brown mixture of nitric oxide and nitrogen dioxide (or tetroxide, p. 350),

$$N_2O_3 \longleftrightarrow NO + NO_2\,;$$

but apparently this change only takes place in presence of moisture.*

Nitrosyl chloride, $NOCl$, the chloride of nitrous acid, is formed by the combination of chlorine and nitric oxide, and also when nitric and hydrochloric acids are mixed (aqua regia, p. 236),

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

It is obtained as an orange gas when nitrosylsulphuric acid (p. 486) is heated with sodium chloride,

$$SO_2(O{\cdot}NO)OH + NaCl = NOCl + NaHSO_4.$$

On hydrolysis with alkalis, it gives a nitrite and a chloride,

$$NOCl + 2NaOH = NaNO_2 + NaCl + H_2O.$$

Hyponitrous acid, $H_2N_2O_2$ or $H-O-N=N-O-H$, is obtained in the form of its sodium salt when sodium nitrate (or nitrite) is reduced with sodium amalgam (p. 670) and water,

$$2NaNO_3 + 8H = Na_2N_2O_2 + 4H_2O.$$

It is also produced by the interaction of nitrous acid and hydroxylamine,

$$HO{\cdot}NO + NH_2{\cdot}OH \quad HO{\cdot}N:N{\cdot}OH + H_2O.$$

It is a crystalline explosive compound, and is only a weak acid. It decomposes spontaneously even in aqueous solution, giving its anhydride (nitrous oxide) and water.* It forms both normal and acid salts. Its silver salt, $Ag_2N_2O_2$, is insoluble in water.

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* The results of density determinations, made with the very carefully dried gas seem to show that the molecules, N_2O_3, are associated at ordinary temperatures.

NITRIC ACID, HNO_3 OR $\begin{matrix}O\\O\end{matrix}\!\!>\!N-OH$, AND ITS DERIVATIVES.

In the preparation of nitric acid (p. 236) on the large scale, sodium nitrate and sulphuric acid are heated together in cast-iron cylinders or retorts, and the reaction is represented by the equation,

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$

The nitric acid vapour is condensed in a series of earthenware Woulfe's bottles or in a series of vertical earthenware pipes.†

When two molecular proportions of the nitrate are used, a higher temperature is required to complete the double decomposition,

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4,$$

and in the later stages the following changes occur,

$$4NaNO_3 + 4NaHSO_4 = 4Na_2SO_4 + 4NO_2 + 2H_2O + O_2.$$

The nitrogen dioxide (tetroxide) thus produced dissolves in the nitric acid which has already distilled, giving a reddish-brown fuming liquid ('*red fuming nitric acid*') which is often used for oxidising purposes.

Chili saltpetre contains chlorides, and commercial nitric acid therefore may contain chlorine, nitrosyl chloride, and oxides of nitrogen. These impurities may be removed by passing air through the gently heated acid. Sulphuric acid, iodic acid (p. 436), and dissolved salts may also be present, but may be got rid of by distilling the nitric acid.

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* Although nitrous oxide is formed when a solution of hyponitrous acid is heated, and may therefore be regarded as the anhydride of hyponitrous acid, the acid is not produced when nitrous oxide is treated with water.

† In one process the whole operation is carried out under reduced pressure, whereby the reaction is completed at a lower temperature and the decomposition of the nitric acid is avoided.

Aqueous solutions of nitric acid, when distilled under a constant pressure, ultimately give a distillate of constant boiling-point (compare p. 418); the solution obtained under atmospheric pressure boils at 120·5°, and contains 68 per cent. of HNO_3.

Except when nitric acid is used in preparing salts from metals, oxides, hydroxides, carbonates, &c., its employment in the laboratory is principally due to the fact that it is a vigorous oxidising agent. The nature of the reduction product formed from the acid depends not only on the substance which is oxidised but also on other conditions, more especially on the temperature and concentration of the acid. Thus, when copper is treated with concentrated nitric acid, the latter is reduced to nitrogen tetroxide (N_2O_4 or NO_2), whereas with a more dilute acid, nitric oxide is obtained (p. 243).

If different reducing agents are employed and the conditions varied, the following reduction products of nitric acid may be obtained; the equations are merely intended to show the progressive character of the reactions, the extent of the reduction being expressed in terms of hydrogen (footnote, p. 285):

$$2HNO_3 + 2H = N_2O_4 + 2H_2O$$
$$2HNO_3 + 4H = N_2O_3 + 3H_2O \text{ (or } 2HNO_2 + 2H_2O)$$
$$2HNO_3 + 6H = 2NO + 4H_2O$$
$$2HNO_3 + 8H = N_2O + 5H_2O$$
$$2HNO_3 + 10H = N_2 + 6H_2O$$
$$2HNO_3 + 12H = 2NH_2{\cdot}OH + 4H_2O$$
$$2HNO_3 + 14H = N_2H_4 + 6H_2O$$
$$2HNO_3 + 16H = 2NH_3 + 6H_2O.$$

The conditions under which most of these reduction products may be prepared have already been stated.

The final reduction product, namely, ammonia, is produced when a nitrate (or a nitrite) is heated with zinc dust (p. 626) and caustic soda, and the quantity of nitric acid (or of nitrate) in a solution may be estimated with the aid of this reaction, as the ammonia which is formed may be determined volumetrically (p. 268).

Nitric acid oxidises so many compounds that only a few of these can be mentioned. Thus it oxidises sulphur (p. 246), iodine (p. 436), phosphorus (p. 548), antimony (p. 564), tin (p. 592), and carbon,* and except in the case of iodine and sulphur, gives rise to the highest oxide of the element. It oxidises most metals, converting them into their nitrates (p. 245). It oxidises three of the halogen acids, hydrogen sulphide, and most of the metallic sulphides. It oxidises the lower oxides of non-metals and of metals, and also salts derived from the lower metallic oxides, the higher oxides or their derivatives being formed; thus sulphur dioxide is converted into the trioxide, arsenious anhydride into arsenic anhydride (p. 557), and ferrous into ferric salts,

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

Since in many of these oxidations the nature of the products depends on the conditions, the equations which are given in particular cases may represent only some of the more important results of the reaction.

The presence of free or combined nitric acid may be detected by the 'brown-ring' test. The substance is mixed with excess of concentrated sulphuric acid, which liberates nitric acid if a nitrate is present, and a solution of ferrous sulphate is carefully poured on to the surface of the *cold* mixture. The production of a brown or black solution where the two liquids come into contact shows the presence of nitric acid. The nitric acid is reduced by the ferrous sulphate (see above), and the nitric oxide thus produced dissolves in the ferrous sulphate solution, giving a dark liquid, which probably contains the compound $FeSO_4,NO$. On this solution being heated, nitric oxide is liberated (p. 245).

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* A glowing stick of charcoal fixed to a long wire and cautiously dipped into warm red *fuming* nitric acid (p. 529) continues to burn much more vigorously than in the air, and a brown gas (NO_2) is evolved in large quantities. The nitric acid is placed in a beaker, which, for safety, stands in a large glass cylinder.

Free nitric acid may be estimated volumetrically, in absence of other acids, by titration with a standard solution of sodium hydroxide. Combined nitric acid—that is to say, nitrates—may be estimated by the method already mentioned; also by converting the whole of the nitric acid into nitric oxide, and then measuring the volume of gas produced.

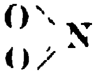
In the latter method, the 'nitrometer,' shown in fig. 101 (p. 476), is used, the bottle (*b*) being disconnected. The nitrometer tube (*c*) is completely filled with mercury by raising the reservoir (*d*), which also contains mercury. A weighed quantity of the nitrate dissolved in the minimum quantity of water is placed in the cup (*g*), and by opening the 3-way tap the solution is run into the nitrometer (the reservoir having been lowered) without admitting air. Concentrated sulphuric acid is then poured into the cup and cautiously run into the nitrometer. The tap having been closed, the contents of the tube are vigorously shaken. The nitric acid, liberated from the nitrate by the sulphuric acid, now reacts with the mercury, and is reduced to *nitric oxide*, the volume of which is subsequently measured under known conditions of temperature and pressure.

The decomposition of the nitric acid is expressed by the equation,

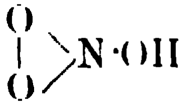
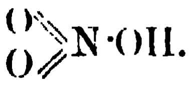
$$2HNO_3 + 3Hg + 3H_2SO_4 = 2NO + 3HgSO_4 + 4H_2O,$$

so that 1 gram-molecule of the acid gives 22·4 litres of nitric oxide at N.T.P.

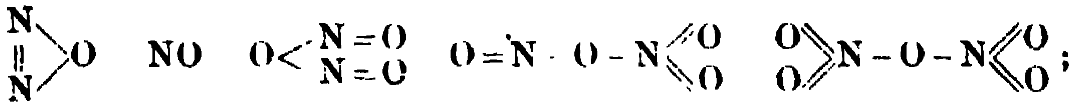
Several of the more important *nitrates* have already been described (pp. 240–242), and the general properties of the nitrates have been noted; other nitrates are mentioned later.

Nitryl chloride, NO_2Cl or  $\genfrac{}{}{0pt}{}{O\diagdown}{O\diagup}N\quad Cl$, is said to be obtained as a yellow liquid (b.p. 5°) by carefully treating pure nitric acid with phosphorus pentachloride (p. 545), and also by the combination of nitrogen tetroxide and chlorine; it is hydrolysed by water, giving nitric and hydrochloric acids.

The Constitution of Nitric Acid and of other Nitrogen Compounds.—The existence of ammonia and of many compounds closely related to ammonia shows that nitrogen may be tervalent. On the other hand, the existence of ammonium chloride and of many other compounds of a similar type shows that the element may be quinquevalent. If now the structure of nitric acid is considered, it may be concluded that the molecule of the acid contains a hydroxyl-group, because the acid is formed by the direct union of its anhydride with water (p. 468).

The structure of the acid, therefore, may be represented by the formula  $\begin{matrix}O\\|\\O\end{matrix}\!\!>N\cdot OH$ or  $\begin{matrix}O\\O\end{matrix}\!\!\gg N\cdot OH$. For reasons similar to those given in discussing the constitution of sulphuric acid (p. 492) the second of these formulæ is usually adopted, and nitrogen in nitric acid and in nitric anhydride is regarded as being quinquevalent. The structure formula of nitrous acid (p. 526) is also based on the evidence that the molecule contains a hydroxyl-group and on considerations of valency.

In the case of the oxides of nitrogen the following formulæ are sometimes employed:



$\begin{matrix}N\\\|\\N\end{matrix}\!\!>O \quad NO \quad O<\begin{matrix}N=O\\N=O\end{matrix} \quad O=N-O-N\begin{matrix}\nearrow O\\\searrow O\end{matrix} \quad \begin{matrix}O\\O\end{matrix}\!\!\gg N-O-N\begin{matrix}\nearrow O\\\searrow O\end{matrix}$;

that of N_2O_4 is based on the fact that this oxide combines with water to give both nitrous and nitric acid, so that it may be regarded as a mixed anhydride (p. 441).

CHAPTER LII.

Phosphorus and its Compounds.

PHOSPHORUS, P_4; AT. WT. 31.

Two important varieties of the element phosphorus are known. One of these, namely, *colourless phosphorus* (often called yellow phosphorus), seems to have been discovered by Brandt in 1669, the other, a much less active form, known as *red phosphorus* (sometimes as amorphous phosphorus), was discovered by v. Schrötter in 1845.

Even the less active variety does not occur in the free state, and the only abundant compounds of the element are certain salts of phosphoric acid, H_3PO_4, more especially *calcium phosphate*, $Ca_3(PO_4)_2$.

This compound is very widely diffused and is present in small quantities in nearly all rock materials and in all *fertile* soils. Phosphates are essential to the life of plants, and the phosphates or other phosphorus compounds contained in plants are equally essential to the life of the higher animals. The brain, nerve tissue, and many other important parts of the animal organism contain complex phosphorus compounds related to the albuminoids (p. 514), and the 'mineral matter' of the bones of vertebrates consists principally of calcium phosphate. Phosphates are excreted by animals; *sodium ammonium phosphate* (p. 548) occurs in the urine, and a large proportion of guano and of coprolites (fossil dung) consists of calcium phosphate.

Calcium phosphate is found in large beds of fossil bones in North America (Florida, South Carolina), and in Algeria; in Spain, as the mineral *phosphorite*.

Apatite is a crystalline mineral consisting of calcium phosphate and calcium chloride or calcium fluoride, and its composition is represented by the formula $3Ca_3(PO_4)_2, CaX_2$, where X represents an atom of chlorine or of fluorine; this mineral is a very common component of rocks, and occurs in large quantities in parts of Canada.

At one time all commercial phosphorus was made from the calcium phosphate contained in bones. The bones were strongly heated in the air in order to burn away the organic matter contained in them, and the crushed product, *bone-ash*, consisting principally (83 84 per cent.) of calcium phosphate, was treated with dilute sulphuric acid in order to convert the calcium phosphate into phosphoric acid,

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4.$$

The solution of the acid was then decanted from the precipitated calcium sulphate, evaporated to a syrup, and mixed with charcoal or coke, after which the pasty mass was dried and heated to a dull red heat; under these conditions the phosphoric acid was converted into metaphosphoric acid (p. 547),

$$H_3PO_4 = HPO_3 + H_2O.$$

The mixture of metaphosphoric acid and carbon was finally heated at a very high temperature in bottle-shaped iron vessels; phosphorus then distilled over, together with carbon monoxide and hydrogen, and the vapour was condensed in receivers containing warm water. In this process it may be supposed that the metaphosphoric acid decomposes into its anhydride P_2O_5 and water,

$$2HPO_3 = H_2O + P_2O_5,$$

and at the very high temperature employed both these products are reduced by carbon,

$$2P_2O_5 + 10C = P_4 + 10CO$$
$$2H_2O + 2C = 2CO + 2H_2;$$

the final results are expressed by the equation,

$$4HPO_3 + 12C = P_4 + 12CO + 2H_2.$$

Phosphorus is now prepared by heating an intimate mixture of calcium phosphate (fossil or mineral phosphate, also bone-ash), sand, and carbon at a very high temperature in an electric furnace (p. 299). The calcium phosphate is decomposed by the silica, giving calcium silicate and phosphorus pentoxide,

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5,$$

and the latter is then reduced by the carbon with formation of phosphorus and carbon monoxide,

$$2P_2O_5 + 10C = P_4 + 10CO.$$

The phosphorus vapour is passed into a copper receiver containing warm water, and the liquid phosphorus is then run into cold water.

The product contains lower oxides of phosphorus and other impurities; it is agitated with a warm dilute solution of potassium dichromate and sulphuric acid, in order to convert these impurities into soluble compounds, and the liquid phosphorus is then usually cast into sticks.

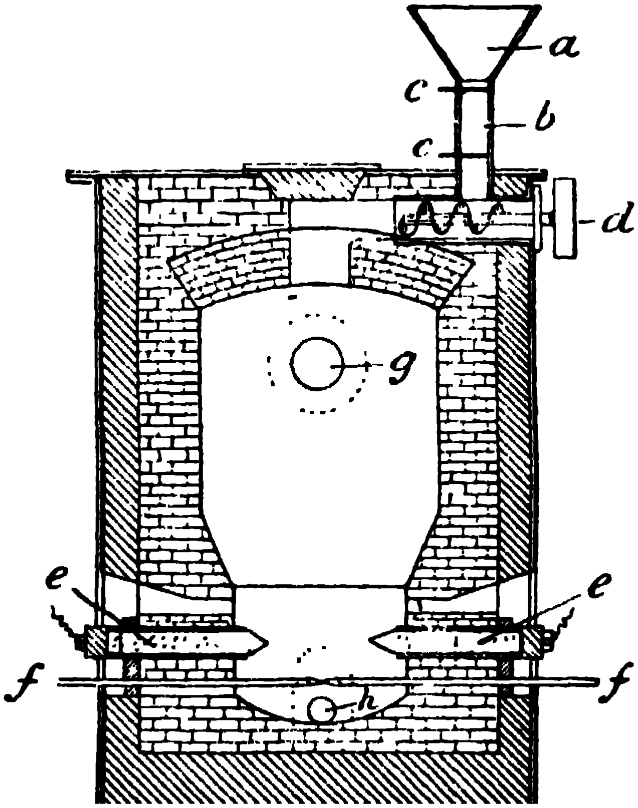


Fig. 105.

A form of electric furnace used in the manufacture of phosphorus is shown in fig. 105. The material is introduced into the hopper (*a*), whence it is passed into the small ante-chamber (*b*), the top and bottom of which consist of movable plates (*c*, *c*); from this chamber it is forced into the furnace by means of the screw (*d*). The carbon electrodes (*e*, *e*) pass through metal casings which are connected to the poles of an alternating dynamo. At the commencement of the operation, instead of these electrodes much smaller rods (*f*, *f*) are used; the latter are pushed through channels in the walls of the furnace, and are withdrawn again when the resistance of the furnace contents has diminished sufficiently to enable the current to pass between the larger electrodes. The gases and vapours escape through the tube (*g*), and the phosphorus is condensed in copper receivers; the fused mass of calcium silicate, &c., flows away through the opening (*h*).

Colourless phosphorus, the variety of the element prepared as described above, is (when pure) a translucent, waxy, crystalline solid, which soon becomes superficially yellow on exposure to light owing to the formation of traces of red phosphorus. It melts at 44° and boils at about 290°; its sp. gr. is 1·84. It is generally kept under water, in which it is insoluble, as it is very liable to take fire spontaneously on exposure to the air at ordinary temperatures.*

Red phosphorus, a dull purple-red crystalline solid, of sp. gr. 2·2, often spoken of as amorphous phosphorus, is very slowly formed when colourless phosphorus is heated at about 250° out of contact with the air.

This may be shown by suspending a small hermetically sealed glass tube containing a little colourless phosphorus in the vapour of boiling diphenylamine (b.p. 310°); if the diphenylamine is *gently* boiled in a long-necked flask a condenser is not required.

Red phosphorus is prepared commercially by heating colourless phosphorus at about 250° in a glass or porcelain vessel, which is embedded in sand contained in an iron pan; the vessel containing the phosphorus is provided with an air-tight cover through which passes a tube with its free end dipping under water. When most of the air has been expelled from the vessel by the application of heat, this tube is closed with a tap and the phosphorus is heated until the change into the red form is practically complete.

The product is ground to a paste with water, boiled with sodium hydroxide solution in order to extract unaltered, colourless phosphorus (see p. 538), washed with water, and dried.

The change from colourless to red phosphorus takes place very slowly at 250°, but in presence of a little iodine (which forms phosphorus iodide) it occurs rapidly at 180° and slowly even at ordinary temperatures. The iodine, or phosphorus iodide, acts as a catalytic agent.

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* Compare footnote, p. 84, as to the danger of handling phosphorus.

Colourless and red phosphorus differ from one another in a very striking manner both in physical and in chemical properties, some of the more important differences are summarised below.

Colourless (Yellow) Phosphorus.	Red Phosphorus.
Very readily soluble in carbon disulphide and soluble in many other carbon compounds.	Insoluble in all liquids.
Melts at 44 , and immediately takes fire when melted in the air.	Melts at about 550° when quickly heated in absence of air; takes fire at about 240° in the air.
Combines slowly with atmospheric oxygen at ordinary temperatures, showing phosphorescence (p. 540).	Does not change when exposed to the air.
Dissolves chemically in hot sodium hydroxide solution, giving phosphine (p. 541).	Insoluble in, and not acted on by, hot sodium hydroxide solution.
Very poisonous.	Non-poisonous.

In spite of these great differences, the two varieties of phosphorus are composed of the same matter, and may be converted one into the other without undergoing any change in weight. Colourless phosphorus, hermetically sealed in a glass tube containing nitrogen or some other inert gas, is transformed into red phosphorus at 250°. Red phosphorus under similar conditions, but at higher temperatures, is converted into a vapour which, when cooled, gives colourless phosphorus. Equal weights of the two forms separately burned in excess of dry oxygen give equal weights of phosphorus pentoxide.

Concerning the relationship between these two forms of the element phosphorus, it may first be noted that from determinations of the vapour densities of many phosphorus compounds, such as phosphine and phosphorus trichloride, the atomic weight of phosphorus, based on its equivalent, is known to be 31. The density of phosphorus vapour (between 515° and 1000°) is 62, corresponding with the molecular weight 124; hence the vapour of phosphorus (from either the colourless or the red form) consists of tetratomic molecules, P_4. It has also been found by cryoscopic and ebullioscopic determinations that colourless phosphorus is tetratomic in solution; but as no solvent for red phosphorus is known, its molecular weight in the dissolved state cannot be determined. The relationship between the two solid varieties of phosphorus, therefore, is unknown.

It may be that the molecules of red, are different from those of colourless, phosphorus, as those of oxygen differ from those of ozone (p. 466); or that the two forms consist of identical molecules which are differently arranged in the two crystalline substances, as probably is the case with the rhombic and monoclinic forms of sulphur.

Whatever the difference may be, it is known that red phosphorus is much the more stable form, and that the transformation of colourless into red phosphorus is accompanied by a very considerable development of heat; as, however, red phosphorus is not a definite substance, but is probably a solution of colourless in 'metallic' phosphorus, or a mixture of several varieties of red phosphorus, the development of heat is not constant, and even the ordinary properties of red phosphorus depend on its method of preparation. *'Metallic' phosphorus* (Hittorf's phosphorus) is a dark-red crystalline substance which is formed when colourless phosphorus is heated with lead at high temperatures; it resembles red phosphorus in properties.

Colourless phosphorus emits a faint, pale greenish-yellow light, which is visible only in the dark, when it is exposed to (atmospheric) oxygen; from this phenomenon, termed *phosphorescence*, the element derives its name.*

The phosphorescence is due to atmospheric oxidation. It seems probable that phosphor*ous* anhydride is first formed, and that this compound then combines with oxygen to form phosphoric anhydride with development of light and heat. Other products (ozone, hydrogen peroxide) are also formed, and a characteristic garlic-like odour is observed.

Colourless phosphorus may be detected by boiling it, or any substance suspected of containing it, with water, in a flask provided with a long glass tube; in the dark a pale, greenish-yellow phosphorescence is seen where the steam containing phosphorous vapour and rising in the tube comes into contact with the air.

Colourless phosphorus is a very active element; it burns in the air (p. 92) and in chlorine (p. 141), combines explosively with bromine (p. 411), unites vigorously with iodine, and so on; it gives three compounds with sulphur, and unites with certain metals, forming *phosphides*. Red phosphorus, of course, gives the same compounds as colourless phosphorus, but not so readily.

The principal use of phosphorus is for making matches.

Ordinary matches, which strike on sandpaper or on any rough surface, consist of strips of wood coated with paraffin-wax, the heads being made of a paste of colourless phosphorus, gum, and red-lead (or some other oxidising agent such as lead dioxide, lead nitrate, &c.). The heads of safety-matches may consist of a mixture of antimony sulphide, potassium chlorate, and gum, and are rubbed on a surface of a mixture of red phosphorus, antimony sulphide, powdered glass, and glue; but many different preparations are used. The principle in all cases is that the heat developed by friction starts a vigorous chemical change.

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* When a solution of colourless phosphorus in carbon disulphide is poured on filter-paper, the solvent rapidly evaporates, and the thin layer of phosphorus thus formed oxidises so rapidly that it takes fire; in the dark, phosphorescence is distinctly observed just before the phosphorus inflames.

HYDRIDES OF PHOSPHORUS.

Phosphorus and hydrogen combine even less readily than do nitrogen and hydrogen; nevertheless several hydrides of phosphorus are known.

Phosphine (*hydrogen phosphide*), PH_3, is formed when calcium phosphide* is placed in water,

$$Ca_3P_2 + 6H_2O = 2PH_3 + 3Ca(OH)_2,$$

and also when colourless phosphorus is heated with a solution of potassium hydroxide (see below),

$$P_4 + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2.\dagger$$

It is a colourless, very poisonous, disagreeably smelling gas, and is only sparingly soluble in water, in which respect it differs widely from ammonia; it burns in the air, giving phosphoric acid,

$$2PH_3 + 4O_2 = 2H_3PO_4,$$

and is readily decomposed into its elements when it is heated out of contact with oxygen.

Phosphine combines with the halogen acids, giving compounds of the formula PH_3, HX or PH_4X, where X represents an atom of a halogen. These compounds are called *phosphonium* salts, as they are of the same type as the ammonium salts, but they are very unstable and are decomposed by water, with liberation of phosphine.

Phosphonium iodide, PH_4I, is the most stable and the best-known phosphonium salt; it is a colourless crystalline substance, which is often produced (owing to the occurrence of secondary reactions) in the preparation of hydrogen iodide from iodine, red phosphorus, and water (footnote †, p. 422).

Liquid hydrogen phosphide, P_2H_4, is formed, together with phosphine and potassium hypophosphite, when colourless phosphorus is heated with potassium hydroxide solution; as the liquid phosphide takes fire spontaneously on exposure to the air, the preparation of phosphine is carried out in the apparatus shown in fig. 106, the air in the flask being first displaced by coal-gas. When the bubbles of gas rise to the surface of the warm water* in the trough they take fire spontaneously and 'smoke-rings' of fumes of phosphoric acid are formed.

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* Calcium phosphide is obtained in a very impure state as a brown powder by gradually adding phosphorus to heated lime. The gas produced when the phosphide is thrown into water takes fire spontaneously.

† Potassium hypophosphite (p. 551).

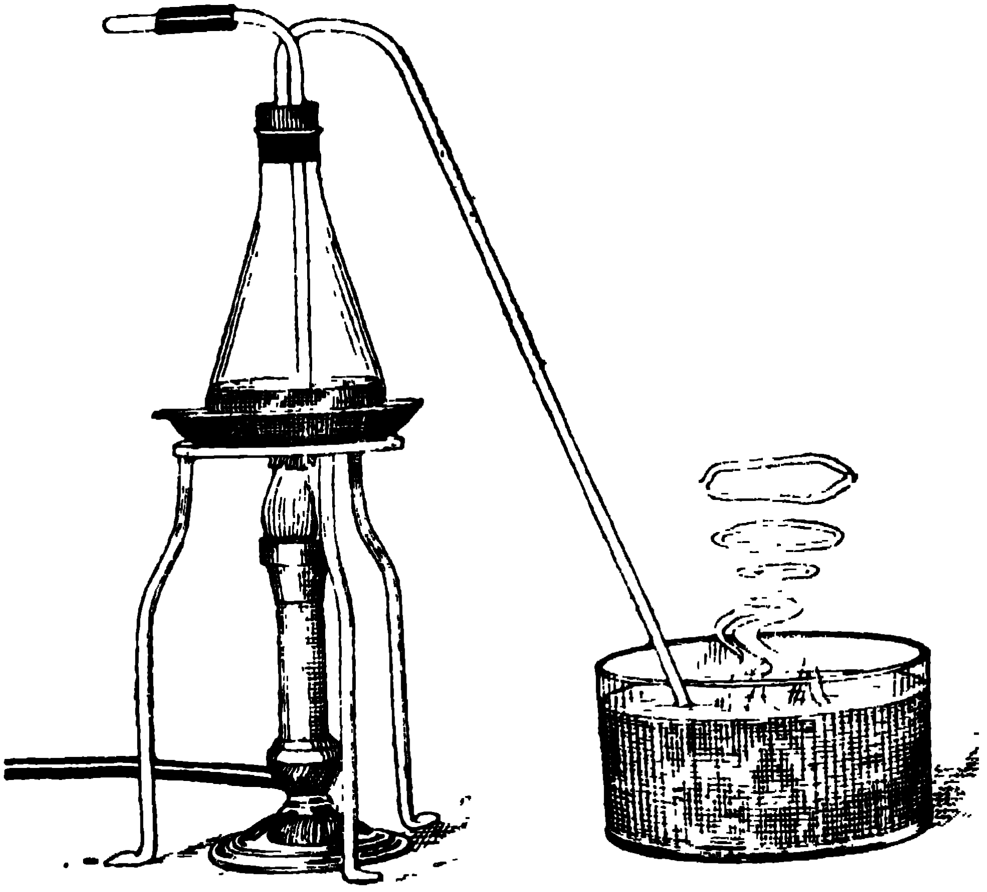

Fig. 106.

A similar spontaneously inflammable product is obtained by the action of water on calcium phosphide. From such mixtures most of the liquid hydride may be separated by passing the gas through well-cooled U tubes.

One or more solid hydrogen phosphides are also known.

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* Unless the water is warm the end of the delivery-tube may get choked up with phosphorus.

HALOGEN COMPOUNDS OF PHOSPHORUS.

Phosphorus combines readily with all the halogens, forming compounds of the type PX_3 or PX_5, in which the phosphorus is either ter- or quinque-valent; it also gives rise to oxyhalogen compounds such as *phosphorus oxychloride*, $POCl_3$, which may be regarded as derivatives of phosphoric acid, $PO(OH)_3$.

The halogen compounds are all obtained by the direct combination of their constituent elements, and the only difficulty in preparing them consists in moderating the violence of the reaction. When excess of phosphorus is used the compound of the type PX_3 is obtained; but when excess of halogen is present this product is converted into one of the type PX_5, except in the case of the *iodide*. The more important halogen derivatives are the following:

Phosphorus trichloride, PCl_3.	Phosphorus tribromide, PBr_3.
Phosphorus pentachloride, PCl_5	Phosphorus pentabromide, PBr_5.

Phosphorus tri-iodide, PI_3.

Phosphorus trichloride, PCl_3, is prepared by passing dry chlorine over colourless phosphorus until all the solid disappears; the product is then purified by distillation.

The phosphorus is placed in a retort (fig. 107) connected with a receiver, and the air in the apparatus is displaced by dry carbon dioxide; a stream of dry chlorine is then led into the retort. A development of heat occurs, and most of the trichloride volatilises; as soon as the phosphorus has disappeared the retort is gently heated (on a water-bath), in order to distil the rest of the product, and the whole is then purified by distillation. The larger wash-bottle, which contains sodium hydroxide solution, serves merely to prevent the escape of chlorine or phosphorus trichloride into the room. Phosphorus trichloride is a mobile liquid (b.p. 76°), having a pungent, very disagreeable smell; it fumes in the air, and when poured into water is vigorously hydrolysed, giving hydrochloric and phosphor*ous* acids (p. 551),

$$PCl_3 + 3H_2O = 3HCl + P(OH)_3.$$

Phosphorus tribromide, PBr_3, may be prepared by *gradually* adding bromine, which is dissolved in carbon disulphide (in order to moderate the reaction) to dry red phosphorus until the latter disappears; the product is separated from the solvent by fractional distillation. It boils at 175°, and resembles the trichloride.

Phosphorus tri-iodide, PI_3, is prepared by gradually adding iodine to colourless phosphorus, both the elements being dissolved in carbon disulphide; the product remains as a red solid when the solvent is distilled off.

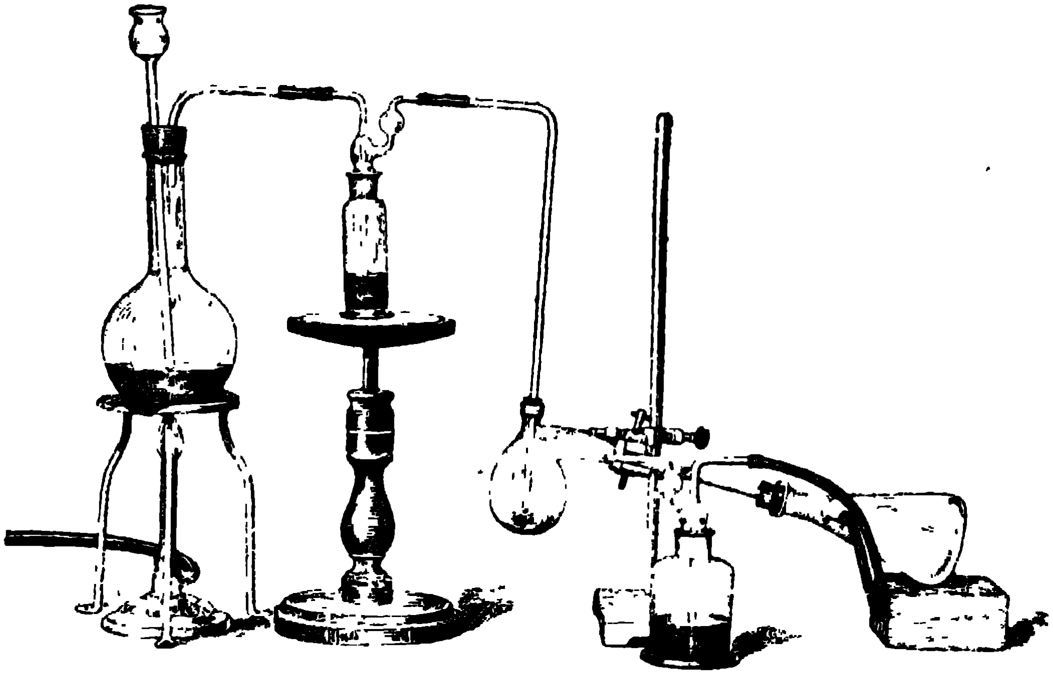


Fig. 107.

Phosphorus pentachloride, PCl_5, is obtained by treating phosphorus with excess of chlorine, and is prepared by passing dry chlorine over the surface of the trichloride; an apparatus like that shown in fig. 107 is used. The pentachloride is a colourless crystalline solid, which sublimes and dissociates (p. 366) when it is heated,

$$PCl_5 \longleftrightarrow PCl_3 + Cl_2.$$

It is violently hydrolysed by water, giving hydrochloric and phosphoric acids,

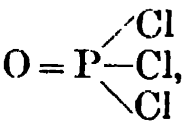
$$PCl_5 + 4H_2O = 5HCl + H_3PO_4.$$

It may be supposed that in this change each of the chlorine atoms is displaced by a hydroxyl-group, giving the unstable compound $P(OH)_5$, which immediately loses the elements of water, giving $PO(OH)_3$.

Phosphorus pentabromide, PBr_5, is obtained by adding bromine to the tribromide; it is a yellowish crystalline solid, similar to the pentachloride in chemical properties.

Phosphorus trifluoride, PF_3, and the *pentafluoride*, PF_5, are colourless gases; a red crystalline iodide, P_2I_4, is known.

The tri- and penta-halogen derivatives of phosphorus are important reagents, as they are used for preparing many halogen compounds. When a substance which contains one or more hydroxyl-groups is treated with one of these phosphorus halides, each of the hydroxyl-groups is displaced by an atom of halogen. Thus water, $H-OH$, gives a halogen acid, $H-X$; nitric acid, $NO_2{\cdot}OH$, gives nitryl chloride, NO_2Cl; sulphuric acid, $SO_2(OH)_2$, gives sulphuryl chloride, SO_2Cl_2 (p. 492); alcohol (p. 126), which has the formula, $C_2H_5{\cdot}OH$, gives ethyl chloride, C_2H_5Cl; and so on.

Phosphorus oxychloride, $POCl_3$ or  $O=P\begin{smallmatrix}\diagup Cl\\ -Cl\\ \diagdown Cl\end{smallmatrix}$, is formed when water is very cautiously added to phosphorus pentachloride until the solid disappears,

$$PCl_5 + H_2O = POCl_3 + 2HCl\,;$$

the product is isolated by fractional distillation. It is a very disagreeably smelling liquid (b.p. 107°), which is rapidly hydrolysed by water, giving hydrochloric and phosphoric acids,

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl.$$

Phosphorus oxybromide, $POBr_3$, is a crystalline solid prepared from the pentabromide in a similar manner.

OXIDES AND OXY-ACIDS OF PHOSPHORUS.

Phosphorus combines very readily with oxygen, and forms several oxides, but none of these is a basic oxide. The only important oxide is phosphorus pentoxide, P_2O_5, the highest oxide of phosphorus. This substance is an anhydride, and corresponding with it are three oxy-acids of phosphorus, which are described below.

Phosphorus pentoxide or **phosphor*ic* anhydride,** P_2O_5, is obtained when phosphorus is burnt in the air; when the supply of oxygen is limited some red phosphorus and lower oxides of phosphorus are also formed; but these impurities may be oxidised to the pentoxide by subliming the impure product in a stream of dry oxygen.

It is a colourless solid which sublimes at high temperatures. Its use in the laboratory for drying gases (p. 85) and liquids depends on the fact that it combines very readily with water to form metaphosphoric acid (see below).

Phosphorus trioxide or **phosphor*ous* anhydride,** P_2O_3, is formed when phosphorus is burnt in a *limited* supply of air. It is a colourless solid (m.p. 22·5°), but it boils at relatively low temperatures (173°), and is therefore easily separated from any pentoxide (which may be formed with it) by distillation in a dry atmosphere.

It combines with cold water, but only slowly, giving phosphorous acid (p. 551).

The vapour density of phosphorus pentoxide corresponds with that required by the molecular formula P_4O_{10}, and that of phosphorus trioxide corresponds with the formula P_4O_6; as the substances are generally called by the names just used, the simpler formulæ P_2O_5 and P_2O_3 are commonly employed. This is all the more permissible because it is possible to regard the existence of the more complex molecules P_4O_6 and P_4O_{10} as examples of association (p. 384).

Phosphorus tetroxide, P_2O_4, is formed, together with phosphorus, when the trioxide is heated at 400°; it is crystalline, and with water it gives phosphorous and phosphoric acids.

THE PHOSPHORIC ACIDS.

Phosphoric anhydride combines with water, giving a monobasic acid, which is called *meta*phosphoric acid,

$$P_2O_5 + H_2O = 2HPO_3.$$

When this acid is boiled with water it is slowly converted into a tribasic acid, known as *ortho*phosphoric acid,

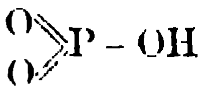
$$HPO_3 + H_2O = H_3PO_4.$$

When orthophosphoric acid is heated at about 255° it loses the elements of water and gives a tetrabasic acid, *pyro*phosphoric acid,

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

As these three acids are all derived from one and the same anhydride, they all contain phosphorus in the particular stage of oxidation in which it exists in this, its highest, oxide. Consequently, in order to distinguish between the different acids, the prefixes *ortho-*, *meta-*, and *pyro-* are employed.

The only approach to a system in the use of the terms ortho- and meta- has already been pointed out; the term pyro- used here and in other cases is an indication that the compound in question was first obtained by a reaction which involved the application of heat.

Metaphosphoric acid, HPO_3 or  $\begin{matrix} O \\ O \end{matrix}\!\!>\!P-OH$, is obtained as a vitreous solid when phosphoric anhydride is left in moist air. It is soluble in water, and when its solution is neutralised with sodium carbonate, **sodium metaphosphate,** $NaPO_3$, is formed. With this solution, silver nitrate gives a colourless precipitate of **silver metaphosphate,** $AgPO_3$.

Metaphosphoric acid gives rise to several different series of salts which are derived from polymeric forms (p. 583) of HPO_3, such as $(HPO_3)_2$, $(HPO_3)_3$, and $(HPO_3)_6$.

Orthophosphoric acid, H_3PO_4 or $O=P(OH)_3$ (commonly called phosphoric acid), is formed when metaphosphoric acid is boiled with water; also when phosphorus (colourless or red) is warmed with nitric acid until it is completely oxidised. In the latter method, the unchanged nitric acid is afterwards expelled by evaporating the solution and then repeatedly adding a little water and evaporating after each addition.

Phosphoric acid is crystalline, deliquescent, and very soluble in water; the solution shows the ordinary properties of a weak acid. The acid is not volatile; at very high temperatures it is converted into metaphosphoric acid, which only volatilises at a bright red heat. Owing to its non-volatility phosphoric acid cannot be prepared from its salts by merely heating the latter with sulphuric acid (p. 359), although these salts are easily decomposed by sulphuric acid.

Phosphoric acid gives three series of salts which are distinguished as primary, secondary, and tertiary phosphates. The tertiary phosphates are normal salts, but the secondary and primary phosphates are acid salts (p. 258). As examples, the names and formulæ of the sodium and calcium salts are given below:

Normal (or *tertiary*).	*Secondary*.	*Primary*.
Na_3PO_4 Sodium phosphate	Na_2HPO_4 Disodium hydrogen phosphate	NaH_2PO_4 Sodium dihydrogen phosphate
$Ca_3(PO_4)_2$ Calcium phosphate.	$CaHPO_4$ Calcium hydrogen phosphate.	$Ca(H_2PO_4)_2$ Calcium dihydrogen phosphate.

Salts which contain two different metals or metallic radicles may also be obtained. Thus **sodium ammonium hydrogen phosphate,** $Na(NH_4)HPO_4, 4H_2O$, is a fairly common substance (known as *microcosmic salt*) in which one hydrogen atom of the acid has been displaced by the univalent sodium atom, another by the univalent ammonium radicle. *Magnesium ammonium phosphate*, $Mg(NH_4)PO_4$, is a well-known compound produced by displacing two of the hydrogen atoms by the divalent magnesium atom and one by the ammonium radicle.

When the acid phosphates (primary or secondary) are strongly heated, they decompose with loss of the elements of water; the primary salts are thus converted into metaphosphates,

$$NaH_2PO_4 = NaPO_3 + H_2O$$
$$Ca(H_2PO_4)_2 = Ca(PO_3)_2 + 2H_2O,$$

and the secondary salts into normal pyrophosphates,

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Salts containing the ammonium radicle are also decomposed when they are strongly heated; microcosmic salt, for example, gives sodium metaphosphate, while magnesium ammonium phosphate gives magnesium pyrophosphate,

$$NaNH_4HPO_4 = NaPO_3 + NH_3 + H_2O$$
$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

Disodium hydrogen phosphate, Na_2HPO_4, is one of the better-known phosphates. It would not be prepared by *neutralising* phosphoric acid with sodium hydroxide (because the solution becomes neutral to litmus when it contains a mixture of Na_2HPO_4 and NaH_2PO_4), but by mixing 1 gram-molecule of sodium carbonate with 1 gram-molecule of phosphoric acid in aqueous solution, and then evaporating; on the solution cooling the salt separates in hydrated crystals, Na_2HPO_4, $12H_2O$. Its solution is used in the laboratory, principally in testing for magnesium salts.

Silver phosphate, Ag_3PO_4, is obtained as a yellow precipitate on a solution of silver nitrate being added to a solution of disodium hydrogen phosphate,

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

As it is chemically soluble in nitric acid, and nitric acid is produced in this reaction, precipitation of the phosphoric acid is incomplete. Silver phosphate also dissolves chemically in ammonium hydroxide solution.

Calcium phosphate, $Ca_3(PO_4)_2$, is the most important salt of phosphoric acid (p. 534); it is insoluble in water, but is converted into soluble acid salts or into phosphoric acid when it is treated with hydrochloric acid or other strong acids,

$$Ca_3(PO_4)_2 + 2HCl \longleftrightarrow 2CaHPO_4 + CaCl_2$$
$$Ca_3(PO_4)_2 + 4HCl \longleftrightarrow Ca(H_2PO_4)_2 + 2CaCl_2.$$

The addition of a soluble basic hydroxide or carbonate to such solutions results in the re-precipitation of the normal calcium salt.

Calcium phosphate is used in agriculture as a source of the phosphorus which is essential to plant-life.

As the normal phosphate, being insoluble in water, would not be carried down by rain to the roots of the crops, the normal salt is transformed into soluble calcium dihydrogen phosphate by treating it with sulphuric acid,

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4.$$

The mixture of salts thus obtained is sold under the name of *superphosphate of lime.*

Magnesium ammonium phosphate, $Mg(NH_4)PO_4$, is obtained as a colourless crystalline precipitate when a solution of a soluble phosphate is treated with a solution of 'magnesia mixture' (a solution of ammonium hydroxide, ammonium chloride, and magnesium sulphate). This compound is used in the *estimation* of phosphoric acid, and is weighed as magnesium pyrophosphate, into which it is converted when it is strongly ignited (p. 549).

Pyrophosphoric acid, $H_4P_2O_7$, is a crystalline compound, which is decomposed by hot water, giving phosphoric acid. It is much more stable in the form of its salts, which are prepared by the methods indicated above.

All the acids derived from phosphoric anhydride, and the salts of these acids, give with *excess* of a boiling solution of ammonium molybdate in nitric acid (p. 513) a canary-yellow precipitate; this reaction serves as a delicate test for phosphates, but a precipitate of similar *appearance* is also given by arsenates (p. 558).

The composition of this precipitate is roughly represented by the formula $11MoO_3, (NH_4)_3PO_4, 6H_2O$, and, as this compound is soluble in phosphoric acid, a large proportion of ammonium molybdate must be added to the solution to be tested, otherwise no precipitate is formed. All the other acids of phosphorus give this reaction, as they are oxidised to phosphoric acid by the nitric acid present.

Phosphorous acid, H_3PO_3, may be formed from its anhydride **(p. 546),** but is prepared by adding phosphorus trichloride to cold water (p. 543) and then evaporating the solution. It is crystalline, and forms salts which are known as the *phosphites.*

Hypophosphorous acid, H_3PO_2, or $H_2PO{\cdot}OH$, is obtained in the form of its potassium or barium salt when colourless phosphorus is heated with an aqueous solution of potassium hydroxide (p. 541) or barium hydroxide,

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 3(H_2PO{\cdot}O)_2Ba + 2PH_3.$$

The solution of the barium salt is treated with dilute sulphuric acid just sufficient to precipitate all the barium as the insoluble sulphate, and the filtered solution of the acid is then evaporated.

Hypophosphorous acid is crystalline and is a monobasic acid. This latter fact seems to show that the molecule only contains one hydroxyl-group, as indicated by the above formula.

Phosphorous and hypophosphorous acids are very active reducing agents, as they are both readily oxidised to phosphoric acid; they both precipitate gold, silver, and mercury (as metals) from solutions of their salts, and even reduce sulphurous acid to sulphur. They both give phosphine and phosphoric acid when they are strongly heated,

$$4P(OH)_3 = PH_3 + 3H_3PO_4$$
$$2H_3PO_2 = PH_3 + H_3PO_4.$$

Hypophosphoric acid, H_2PO_3, is formed, together with phosphorous and phosphoric acids, by the atmospheric oxidation of moistened phosphorus; it is decomposed by hot mineral acids, giving phosphorous and phosphoric acids.

CHAPTER LIII.

Arsenic and its Compounds.

ARSENIC, As_4; AT. WT. 75.

Arsenic, although related to phosphorus, is a much less active element even than red phosphorus, and in some respects has the properties of an ordinary metal. It occurs in nature in the free state, sometimes in distinct crystals, but is principally found in combination with sulphur as the red mineral *realgar*, As_2S_2, and the yellow mineral *orpiment*, As_2S_3; *arsenical pyrites* or *mispickel*, FeS_2, $FeAs_2$[*], and *white arsenic*, As_2O_3, also occur.

The free element is not of much practical importance. It is prepared by heating arsenical pyrites alone, or by heating arsenious oxide with charcoal; in the former case the arsenical pyrites decomposes into arsenic and ferrous sulphide (FeS), whereas in the latter the oxide is reduced with formation of arsenic and carbon monoxide. The liberated arsenic volatilises and is condensed in suitable receivers.

The element thus obtained is a steel-gray crystalline, brittle substance of sp. gr. 5·7. It sublimes at high temperatures, giving a yellow vapour, which consists of tetratomic molecules, As_4; at a white heat these molecules undergo dissociation. Arsenic is insoluble in water, and is not acted on appreciably by hot hydrochloric acid, but it is readily oxidised by concentrated nitric acid, with formation of arsenic acid (p. 558). It oxidises superficially on exposure to moist air, and burns when it is heated in oxygen, giving arsenious anhydride. It combines readily with the halogens.

Arsenic exists in three varieties. When the element is heated in a stream of hydrogen or carbon dioxide it sublimes

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[*] The composition of this substance may also be represented by the formula $FeSAs$ or $Fe(S,As)_2$; in the latter case, the formula indicates that *some* of the sulphur has been displaced by arsenic, or *vice versâ*.

(rapidly at about 450°), and is deposited near the source of heat in silvery crystals (ordinary arsenic); farther from the source of heat a black, lustrous crystalline deposit (sp. gr. 4·7) is formed, and farther still a yellow crystalline deposit (sp. gr. 3·9). The yellow form is soluble in carbon disulphide, and from ebullioscopic determinations it is found that its molecular formula is As_4.

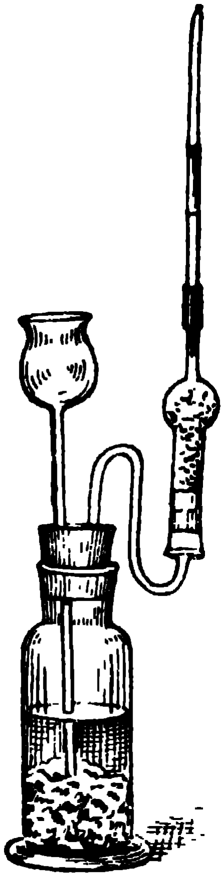

Fig. 108.

Arsine or **hydrogen arsenide,** AsH_3, is not formed when arsenic and hydrogen are heated together, but is easily obtained, mixed with a large proportion of hydrogen, by treating arsenic compounds with zinc and hydrochloric or dilute sulphuric acid. Under these conditions most arsenic compounds are probably first transformed into arsenious acid, H_3AsO_3, or arsenic acid, H_3AsO_4, as the case may be, and these compounds are then reduced; the reactions, therefore, may be expressed by equations such as,

$$H_3AsO_3 + 6H = AsH_3 + 3H_2O$$
$$H_3AsO_4 + 8H = AsH_3 + 4H_2O.$$

The formation and some of the properties of arsine are easily demonstrated in the following manner; but as the gas is highly poisonous great care should be taken not to inhale any of it, and the experiments should be carried out in a draught cupboard.* Hydrogen is generated from zinc and dilute sulphuric acid in the apparatus shown in fig. 108, and is dried with the aid of the small calcium chloride tube. When it has been proved that the air has been expelled from the apparatus (p. 102), *but not before* this has been done, the escaping hydrogen is lighted at the outlet. A small quantity of arsenious anhydride, say 0·01 gram, is then dissolved in

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* Similar precautions should be observed in working with other volatile compounds of arsenic, and also with those of antimony and mercury.

1–2 c.c. of dilute hydrochloric acid, and some of the solution is poured down the thistle funnel. Almost immediately the flame becomes pale blue, and 'smoke' rises from it; these changes are due to the presence of arsine, which burns in a plentiful supply of air, forming arsenious anhydride and water,

$$2AsH_3 + 3O_2 - As_2O_3 + 3H_2O.$$

Like hydrogen iodide, hydrogen sulphide, ammonia, phosphine, and many other hydrogen compounds, arsine is decomposed into its elements when it is heated alone. This decomposition takes place, to a great extent, in the hydrogen flame (before the arsine inside the flame comes into contact with atmospheric oxygen); and when any cold object, such as a porcelain basin, is slowly passed through the flame, the arsenic vapour contained in the flame is condensed, giving a black, lustrous deposit. That this decomposition of arsine into its elements is easily brought about may be shown by gently heating the outlet-tube near the bottom with a very small Bunsen-flame; a dark mirror or lustrous film is deposited above the heated portion of the tube, and the hydrogen flame loses its bluish colour and no longer smokes.

A distinct mirror may be obtained under the above conditions even when only about 0·01 milligram of arsine is generated, so that by this method or test, known as *Marsh's test*, the presence of any arsenic compound in any material is easily detected. As, however, commercial zinc and commercial sulphuric acid may contain arsenic compounds, the hydrogen evolved from these materials should be carefully examined before adding the substance to be tested. (Compare also footnotes, p. 296.)

Instead of the hydrogen, necessary for the reduction of the arsenic compound, being generated from zinc and an acid in the above manner, it may be generated electrolytically in the solution suspected to contain the arsenic compound; proper precautions being observed, it is said to be possible to detect 0·0000005 gram of combined arsenic in 50 c.c. of a liquid.

Arsine may also be prepared by treating zinc arsenide with hydrochloric acid, just as phosphine may be prepared from calcium phosphide and water,

$$Zn_3As_2 + 6HCl = 2AsH_3 + 3ZnCl_2.$$

Arsine is sparingly soluble in water, does not unite with acids, and is oxidised by a solution of silver nitrate, giving arsenious anhydride (or acid), nitric acid, and silver,

$$2AsH_3 + 12AgNO_3 + 3H_2O = As_2O_3 + 12HNO_3 + 12Ag.$$

Although both silver and arsenious anhydride are acted on by nitric acid, they are not attacked by the acid produced in this reaction, because it is cold and very dilute.

OXIDES OF ARSENIC.

There are two oxides of arsenic which correspond with the two oxides of phosphorus, and like the latter they are both acid-forming oxides or anhydrides; the lower oxide, As_2O_3, is a common and important substance, but the higher oxide, As_2O_5, is hardly met with except in the form of the acid, H_3AsO_4, and its salts.

Arsenious anhydride (arsenic trioxide), As_2O_3, known commercially as 'white arsenic,' is obtained as a by-product in many metallurgical operations. When ores or minerals which contain *arsenides* (compounds of arsenic with a metal) are heated in the air, these compounds are oxidised, and arsenious anhydride volatilises; the vapour is then condensed in chambers or in long flues (p. 586). The crude product is purified by heating it in cylindrical iron retorts, and condensing the vapour in a series of chambers; as these get hot the sublimed anhydride softens, and solidifies on cooling to a vitreous amorphous mass, which at ordinary temperatures very slowly changes into a white, porcelain-like solid, as the result of crystallisation. When arsenious anhydride is slowly heated (in a glass tube) it softens at about 200° and then volatilises; the vapour condenses directly to the solid state, giving a beautiful crystalline sublimate.

The density of this vapour corresponds with that required by the molecular formula As_4O_6, but at high temperatures (above 700°) dissociation occurs and molecules, As_2O_3, are formed; as in the case of the oxides of phosphorus, the complex molecules may be regarded as associated molecules.

When arsenious anhydride is mixed with some dry ground charcoal, and the mixture, covered with a little more charcoal, is heated in a tube (beginning at the top), a lustrous mirror of arsenic is formed, owing to the reduction of the anhydride and the deposition of the element,

$$2As_2O_3 + 6C = As_4 + 6CO.$$

Arsenious anhydride is only very sparingly soluble even in hot water. The solution has an acid reaction to litmus, and doubtless contains arsenious acid,

$$As_2O_3 + 3H_2O = 2H_3AsO_3, \text{ or } 2As(OH)_3;$$

but when evaporated, even at ordinary temperatures, it gives a crystalline deposit of arsenious anhydride, a fact which shows that the acid is very unstable. The anhydride dissolves chemically in solutions of the alkali hydroxides and in those of the alkali carbonates (liberating carbon dioxide), giving salts of **arsenious acid**, which are called **arsenites.**

The arsenites of sodium and potassium are readily soluble in water; but the normal salts of these metals, like the soluble normal phosphates (p. 548), are hydrolysed by water, giving alkaline solutions,

$$As(ONa)_3 + H_2O = As(ONa)_2{\cdot}OH + NaOH.$$

Silver arsenite, $As(OAg)_3$, is formed as a pale-yellow precipitate on silver nitrate being added to a solution of sodium arsenite.

Scheele's green or *mineral green* is manufactured for use as a pigment by gradually adding a solution of copper sulphate to a solution of sodium arsenite, and then washing the precipitate with water; it has approximately the composition $CuHAsO_3$, and may be regarded as copper hydrogen arsenite.

Arsenious anhydride and arsenious acid are mild reducing agents. Thus they reduce nitric acid (see below); they also reduce the halogens to halogen acids in aqueous solution,

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI.$$

In the case of hydrogen iodide the reaction is readily reversible, but not in presence of sodium hydrogen carbonate, which converts the acid into its more stable sodium salt.

$$Na_3AsO_3 + H_2O + I_2 + 2NaHCO_3 = Na_3AsO_4 + 2NaI + 2CO_2 + 2H_2O.$$

A standard solution of arsenious anhydride in excess of sodium bicarbonate is often used for the estimation of iodine (bromine or chlorine), and a standard solution of iodine may be used for the estimation of arsenious anhydride (dissolved in a solution of sodium hydrogen carbonate).

Arsenic anhydride * (arsenic pentoxide), As_2O_5, is much less stable than phosphoric anhydride, and is decomposed at high temperatures into arsenious anhydride and oxygen. It is not formed by heating arsenic or arsenious anhydride in oxygen, but is easily obtained, combined with water, as arsenic acid, by oxidising arsenic or arsenious anhydride with nitric acid or with chlorine water.

Thus, if arsenious anhydride is warmed with excess of nitric acid until a brown gas (p. 528) is no longer evolved, the solution on evaporation gives hydrated crystals of arsenic acid, H_3AsO_4, which when heated just below a red heat decompose into the anhydride and water; the anhydride is a crystalline solid which combines with water to form the acid.

The hydrated crystals of arsenic acid effloresce on exposure to the air, and form **pyroarsenic acid**, $H_4As_2O_7$, which when heated at 200° is converted into **meta-arsenic acid**, $HAsO_3$. These acids are also known in the form of their salts, which are prepared by methods similar to those used in the case of salts of the pyro- and meta-phosphoric acids (p. 549); the salts and the free acids pass into (ortho) arsenates and (ortho) arsenic acid respectively when they are treated with water.

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* The name of the element is pronounced ar′-se-nic, but the acid, H_3AsO_4, is called ar-sen′-ic acid.

Arsenic acid, H_3AsO_4 or $AsO(OH)_3$, is readily soluble in water. In aqueous solution it is an oxidising agent; it oxidises sulphurous acid, for example,*

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4,$$

and also hydrogen sulphide,

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S.$$

These reactions are of practical importance for reasons given later (p. 559).

The normal arsenates of the alkali metals (and of ammonium) are soluble in water, by which, however, they are hydrolysed, as are the soluble normal phosphates (p. 548); the other normal arsenates are insoluble in water, but dissolve chemically in acids.

Silver arsenate, Ag_3AsO_4, is obtained as a reddish-brown precipitate on adding silver nitrate to a solution of an arsenate (in absence of acids),

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

It dissolves chemically in nitric acid and in ammonium hydroxide solution (compare silver phosphate, p. 549).

Arsenic acid (and arsenates) and arsenious acid (and arsenites) give with a solution of ammonium molybdate in nitric acid a canary-yellow precipitate indistinguishable in appearance from that obtained with phosphoric acid (p. 550); but the precipitate does not form quickly unless the solution is heated. In this reaction, arsenious acid, if present, is first oxidised to arsenic acid by the nitric acid.

Magnesium ammonium arsenate, $Mg(NH_4)AsO_4$, is formed from soluble arsenates under the same conditions as magnesium ammonium phosphate is produced from soluble phosphates (p. 550); it is insoluble in water, and gives **magnesium pyroarsenate**, $Mg_2As_2O_7$, when it is heated.

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* This may be shown by adding sulphurous acid to a warm solution containing arsenic acid, barium chloride, and hydrochloric acid; after a few moments the precipitation of barium sulphate begins.

SULPHIDES OF ARSENIC.

There are three well-known sulphides of arsenic, namely, As_2S_2, As_2S_3, and As_2S_5, of which the last two correspond with the oxides As_2O_3 and As_2O_5 respectively.

The disulphide occurs as the mineral *realgar* (p. 552). *Ruby sulphur*, which is manufactured by melting arsenic with sulphur, has approximately the same composition as realgar; when mixed with sulphur and potassium nitrate it gives a powder which burns with a dazzling white light (*Indian fire*, *Bengal lights*).

Arsenic trisulphide or **arsenious sulphide**, As_2S_3, occurs in the crystalline state as orpiment (p. 552), and is obtained as a canary-yellow amorphous precipitate when hydrogen sulphide is passed into a solution of arsenious acid * or of an arsenite to which hydrochloric acid has been added,

$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

It is insoluble in cold hydrochloric acid, but dissolves chemically in a solution of ammonium sulphide, sodium hydroxide, or ammonium carbonate (p. 567). When heated in the air it gives sulphur dioxide and arsenious anhydride.

Arsenic pentasulphide, As_2S_5, is formed when hydrogen sulphide is passed into a warm solution of arsenic acid which contains hydrochloric acid; but as some of the arsenic acid may be reduced to arsenious acid with precipitation of sulphur (see below), the pentasulphide is best prepared by melting the trisulphide with sulphur. It is a yellow solid, insoluble in hydrochloric acid.

Dilute solutions of arsenates, acidified with hydrochloric acid, do not give a precipitate with hydrogen sulphide until after some time has elapsed, and even then the first precipitate is principally sulphur, produced by the oxidation of the hydrogen sulphide (p. 558); on continued treatment arsen*ious* sulphide is thrown down owing to the interaction of the arsenious acid and hydrogen sulphide (p. 559).*

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* A 'colloidal solution' (p. 327) of arsenious sulphide is formed, unless the arsenious acid solution also contains hydrochloric acid.

The behaviour of the sulphides of arsenic towards ammonium sulphide and towards alkali hydroxides is described later.

Arsenic compounds are used in medicine; most of them are highly poisonous, and 'white arsenic' is employed in the manufacture of vermin-poisons, &c. Orpiment is used as an oil-paint. The arsenites and arsenates are used in dyeing and in the colour industry.

The halogen derivatives of arsenic are of the type AsX_3, but fluorine also gives a *pentafluoride*, AsF_5.

Arsenic trichloride, $AsCl_3$, is a colourless liquid (b.p. 130°) prepared by passing chlorine over arsenic (compare PCl_3); it is hydrolysed by water,

$$AsCl_3 + 3H_2O = As(OH)_3 + 3HCl,$$

but the reaction is reversible, and in presence of concentrated hydrochloric acid hydrolysis is incomplete. Consequently, when arsenious anhydride (or arsenious acid) is distilled with concentrated hydrochloric acid, the volatile arsenious chloride slowly but continuously passes over with the acid.

A study of the properties of arsenic brings to light the difficulty of sharply dividing the elements into metals and non-metals.

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* This behaviour of solutions of arsenic acid (or arsenates) is a frequent source of error in qualitative analytical work. When the presence of an arsenate is suspected, the solution should be warmed with sulphurous acid and afterwards boiled to expel sulphur dioxide. In this way the arsenic acid is reduced and the solution then gives an immediate precipitate of arsenious sulphide, unaccompanied by sulphur.

CHAPTER LIV.

Antimony and Bismuth and their Compounds.

ANTIMONY, Sb_2; AT. WT. 120·2.

Antimony is very closely related to arsenic, but it is more metallic in character both as regards physical and chemical properties. It does not occur in the free state to any considerable extent, and the principal source of antimony is *stibnite*, a black, lustrous, crystalline form of antimony trisulphide, Sb_2S_3; the element also occurs as the oxide Sb_2O_3. Antimony is obtained from stibnite by heating the ore with iron in crucibles (made of a baked mixture of graphite and clay), which are placed in a furnace; the sulphide is thus reduced and the melted antimony is poured off,

$$Sb_2S_3 + 3Fe = Sb_2 + 3FeS.$$

Another method is to heat the ore in a reverberatory furnace (p. 587) until the sulphide is partly converted into oxide, with formation of sulphur dioxide; the mixture of the oxide and unchanged sulphide is then heated in crucibles with charcoal and sodium carbonate, whereupon the oxide and sulphide act on one another, giving antimony and sulphur dioxide.* The charcoal reduces any remaining oxide, and the melted sodium carbonate which forms a layer at the surface prevents the volatilisation of the antimony.

Antimony is a bluish-white, lustrous, crystalline substance of sp. gr. 6·7, and is so brittle that it is easily powdered. It melts at 630° and vaporises only at very high temperatures; its vapour probably consists of diatomic molecules, Sb_2. It burns when it is very strongly heated in the air, forming antimony trioxide (and also the tetroxide), and it is oxidised by nitric acid, giving either the trioxide or the acid derived from the pentoxide according to the conditions. It is not attacked by boiling concentrated hydrochloric acid[*] except in presence of air, when it yields antimony trichloride,

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* This principle is applied in the preparation of several metals, as, for example, in the case of lead (p. 593) and copper (p. 651).

$$2Sb_2 + 12HCl + 3O_2 = 4SbCl_3 + 6H_2O.$$

Antimony is used in the preparation of certain alloys mentioned later (pp. 589, 597).

Stibine or **antimony hydride**, SbH_3, is a very poisonous gas,[†] and is formed from antimony compounds in just the same way as arsine is produced from arsenic compounds (p. 553). The formation and properties of stibine may therefore be demonstrated by generating the gas by the reduction of some antimony compound (say 0·05 gram) in Marsh's apparatus (fig. 108, p. 553). Shortly after the antimony solution has been added the flame of the burning hydrogen acquires a bluish-gray appearance, and fumes of antimonious oxide are formed,

$$2SbH_3 + 3O_2 = Sb_2O_3 + 3H_2O.$$

The gas, like arsine, is decomposed when it is heated, and a cold porcelain basin slowly passed through the flame becomes coated with a black film of antimony, rather darker than, and not so lustrous as, the film obtained in the case of arsine. When the glass tube through which the stibine is passing is gently heated, a 'mirror' of antimony is deposited close to the source of heat. Minute quantities of antimony compounds may be thus detected.

The film of antimony obtained on the porcelain basin or in the glass tube may be distinguished from that of arsenic very easily, as it is *insoluble* in a dilute solution of bleaching powder or sodium hypochlorite or nitric acid; the arsenic film disappears when it is treated with one of these reagents because the element is oxidised to arsenic acid.

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[*] Many metals which are not attacked by hydrochloric acid alone are acted on by the acid in the presence of oxygen, the reaction in the latter case being more strongly exothermic owing to the simultaneous oxidation of the nascent hydrogen. (Compare p. 340.)

[†] Compare footnote, p. 553.

Stibine may be prepared by treating *zinc antimonide*, a compound of zinc and antimony, with dilute hydrochloric acid,

$$Zn_3Sb_2 + 6HCl = 2SbH_3 + 3ZnCl_2.$$

The gas obtained in this way may be freed from hydrogen by passing it through a tube cooled in liquid air, when the stibine solidifies. Arsine may be separated from hydrogen in a similar manner.

Stibine, like arsine, decomposes silver nitrate in aqueous solution, but the results are very different; whereas the arsenic in arsine is converted into arsenious anhydride which remains *in solution*, the antimony in stibine is *precipitated* as a black powder (silver antimonide),

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

These reactions may serve for the separation of 'arsenic' from 'antimony' (footnote, p. 428).

ANTIMONY TRIOXIDE AND SALTS DERIVED FROM IT.

Antimony forms two oxides, Sb_2O_3 and Sb_2O_5, which are similar in type to the corresponding oxides of arsenic; but the lower oxide of antimony, unlike arsenious anhydride, is a *basic* oxide, and with acids it gives corresponding salts, the *antimonious salts*, and water. Although a basic oxide, its basic properties are not very decided; in consequence, the antimonious salts are hydrolysed by water, and weak acids, such as carbonic acid, do not give salts with the oxide.

Antimonious oxide or **antimony trioxide**, Sb_2O_3, may be obtained by heating antimony in the air or with dilute nitric acid.

As these products may contain the pentoxide, the pure compound is prepared by boiling antimony oxychloride (see below) with a solution of sodium carbonate, washing the residue ($SbO \cdot OH$) with water, and then igniting it in absence of air.

It is a pale buff-coloured crystalline substance, practically insoluble in water; it volatilises only at very high temperatures, and is easily reduced when it is heated with carbon or in a stream of hydrogen.

Antimony trichloride, $SbCl_3$, is formed when the trioxide (or the trisulphide, p. 566) is dissolved in concentrated hydrochloric acid,

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O;$$

but as it is hydrolysed by water (see below), the pure anhydrous salt is prepared by gently heating an *excess* of antimony in a stream of dry chlorine and then distilling the product.*

It is a soft crystalline substance (m.p. 73°), boiling at 223°, and is sometimes called 'butter of antimony.' It dissolves in concentrated hydrochloric acid; but when this solution is poured into water the trichloride is hydrolysed, giving an insoluble basic salt (p. 510), **antimony oxychloride,** SbOCl,

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

On excess of concentrated hydrochloric acid being added, the above reaction is reversed and the oxychloride is converted into the soluble trichloride.

Antimony trioxide dissolves chemically in an aqueous solution of potassium hydrogen tartrate (p. 283), and on the filtered solution being evaporated colourless crystals of *tartar emetic*, $C_4H_4O_6(SbO)K, \frac{1}{2}H_2O$,† are obtained; this compound is used in dyeing, and in medicine (as an emetic).

ANTIMONY PENTOXIDE, ANTIMONIC ACID, AND ANTIMONY PENTACHLORIDE.

When antimony is warmed with excess of concentrated nitric acid it is converted into a white powder which is insoluble in the acid; a similar insoluble substance is formed when antimony pentachloride (see below) is boiled with a large volume of water. Judged by analogy with phosphorus and arsenic, this product should have the composition, H_3SbO_4,

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* Compare footnote, p. 553.

† This formula merely gives the composition of the salt, and shows that *two* molecules of the tartrate contain *one* molecule of water of hydration.

$$SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl;$$

but the substance actually produced is not constant in composition, and is probably a mixture of **antimonic acid,** H_3SbO_4, and **metantimonic,** $HSbO_3$ (corresponding with metaphosphoric acid). It dissolves chemically in solutions of the alkali hydroxides, giving *antimonates*, and when heated gently it gives a yellow residue of **antimony pentoxide,** or **antimonic anhydride,** Sb_2O_5.

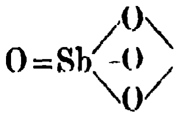
Potassium metantimonate, $KSbO_3$, is produced when antimony is cautiously heated with potassium nitrate; when treated with water it is converted into soluble **potassium dihydrogen pyroantimonate,**

$$2KSbO_3 + H_2O = K_2H_2Sb_2O_7,$$

and this solution gives with a solution of a sodium salt an almost insoluble precipitate of **sodium dihydrogen pyroantimonate,**

$$K_2H_2Sb_2O_7 + 2NaCl = Na_2H_2Sb_2O_7 + 2KCl.$$

Potassium metantimonate, therefore, is occasionally used in testing for sodium salts.

An *oxide* of the composition Sb_2O_4, which may be regarded as *antimonious antimonate*,  $O{=}Sb\begin{smallmatrix}\diagup O \diagdown\\ -O-\\ \diagdown O \diagup\end{smallmatrix}Sb$, that is to say, as the antimony salt of antimonic acid, is known. It is formed when the trioxide or the pentoxide is heated in the air, in the one case with absorption, and in the other with liberation of oxygen.

Antimony pentachloride, $SbCl_5$, is formed when antimony is treated with excess of chlorine, and when chlorine is led over antimony trichloride (compare phosphorus pentachloride); it is purified by distillation, and is a colourless fuming liquid boiling at 140°. Like phosphorus pentachloride, it dissociates when it is strongly heated;* it dissolves in cold water, and may be obtained again from the solution in hydrated **crystals**;

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* Probably this is the reason why the b.p. is lower than that of $SbCl_3$.

but it is decomposed by boiling water, giving antimonic acid (p. 565).

Antimony pentachloride is an acid chloride, and not a salt of hydrochloric acid; it does not yield chlorine when it is warmed with concentrated sulphuric acid and manganese dioxide.

SULPHIDES OF ANTIMONY

Antimony forms two sulphides which are closely related to the corresponding sulphides of arsenic and yet differ from the latter in certain important respects.

Antimony trisulphide, Sb_2S_3, is obtained as an orange-red precipitate when hydrogen sulphide is passed into a solution of an antimonious salt,

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

It is chemically soluble in hot concentrated hydrochloric acid, a property in which it differs from arsenic trisulphide, but like the latter it dissolves chemically in solutions of alkali hydroxides and of ammonium sulphide (see below); it is not acted on by a solution of ammonium carbonate (compare arsenic trisulphide, p. 559).

The great difference in colour between native antimony sulphide (stibnite) and the precipitated sulphide seems to be due to a difference in physical structure; the orange precipitated sulphide, which seems to be amorphous, when melted out of contact with the air gives on cooling the gray crystals of stibnite.

Antimony pentasulphide, Sb_2S_5, is obtained as an apparently amorphous orange-red precipitate when hydrogen sulphide is led into an acid solution of an antimonate; when heated with concentrated hydrochloric acid it gives antimony *tri*chloride, hydrogen sulphide, and sulphur,

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + 2S,$$

and with alkali hydroxides and sulphides it gives the compounds mentioned below.

The behaviour of the sulphides of arsenic and of antimony (and of tin, p 592) towards ammonium sulphide and alkali hydroxides is of some importance, because these reagents are used in separating the sulphides just named from other sulphides which are precipitated by hydrogen sulphide in presence of *dilute* hydrochloric acid. As regards the action of ammonium sulphide, it is important to note that the ordinary *yellow* laboratory reagent contains not only ammonium sulphide, $(NH_4)_2S$, and ammonium hydrosulphide, $(NH_4)HS$ (p. 267), both of which give colourless solutions, but also substances known as ammonium polysulphides; the latter are formed by the combination of the sulphide with sulphur which is produced by the atmospheric oxidation of the hydrosulphide,

$$4(NH_4)HS + O_2 = 2(NH_4)_2S + 2S + 2H_2O,$$

and may be represented by formulæ such as $(NH_4)_2S, S$ or $(NH_4)_2S, S_2$.

Now, just as the trioxide and pentoxide of arsenic, by combination with the elements of hydrogen oxide (water), give rise to arsenious and arsenic acids respectively, so also theoretically the two sulphides of arsenic might give rise to corresponding acids by combination with hydrogen sulphide. These acids would be H_3AsS_3 and H_3AsS_4 respectively: they would contain sulphur in the place of an equivalent quantity of oxygen, but they would be of the same type as arsenious and arsenic acid respectively, and might therefore be called *thio-arsenious acid* and *thio-arsenic acid* respectively.

As a matter of fact, thio-arsenious and thio arsenic acid are not known, but *salts* derived from these acids are actually formed when the tri- and penta-sulphides of arsenic are treated with a solution of ammonium sulphide,

$$As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3,$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

In an exactly similar manner the tri- and penta-sulphides of antimony give rise to salts of *thio-antimonious* and *thio-antimonic acids*,

$$Sb_2S_3 + 3(NH_4)_2S = 2(NH_4)_3SbS_3$$
$$Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4.$$

These compounds are formed when colourless ammonium sulphide is used, but this solution acts on antimony trisulphide only very slowly. When yellow ammonium sulphide is employed, the thio-arsenite and thio-antimonite combine with the sulphur of the ammonium polysulphide (just as arsenites and antimonites take oxygen from certain compounds), and are thus converted into thio-arsenates and thio-antimonates respectively,

$$(NH_4)_3AsS_3 + (NH_4)_2S,S = (NH_4)_3AsS_4 + (NH_4)_2S.$$

Antimony trisulphide is acted on much more readily by yellow ammonium sulphide than by the colourless solution.

When a solution of any of these thio-salts is treated with an acid, the thio-acid is liberated, but it immediately decomposes into hydrogen sulphide and a metallic sulphide, which is precipitated,

$$2H_3AsS_3 = As_2S_3 + 3H_2S$$
$$2H_3SbS_4 = Sb_2S_5 + 3H_2S.$$

These reactions bring out very well the close relationship which exists between oxygen and sulphur in many of their compounds.

When the sulphides of arsenic, antimony, and tin are treated with a solution of an alkali hydroxide, instead of with ammonium sulphide, a mixture of the oxygen acid and the sulphur acid is obtained in the form of their salts; thus arsenic trisulphide gives with potassium hydroxide a mixture of potassium arsenite and potassium thio-arsenite, the formation of which may be expressed as follows:

$$As_2S_3 + 6KOH = 2K_3AsO_3 + 3H_2S$$
$$3H_2S + 6KOH = 3K_2S + 6H_2O$$
$$As_2S_3 + 3K_2S = 2K_3AsS_3,$$

or

$$2As_2S_3 + 12KOH = 2K_3AsO_3 + 2K_3AsS_3 + 6H_2O.$$

Similar reactions occur in other cases.

BISMUTH, Bi_2; AT. WT. 208.

Bismuth is found principally in the free state, but it also occurs combined with sulphur, as *bismuth glance*, Bi_2S_3, and with oxygen as *bismuth ochre*, Bi_2O_3. It may be obtained by simply heating the crushed rock material in which the free metal is contained, and allowing the melted bismuth to run into moulds.

As only the free bismuth is extracted by this process, and many ores contain the combined element, a better process is to heat the ores with charcoal, iron, and some flux (compare antimony, p. 561) in a suitable furnace; the whole of the metal then collects under the slag, and is afterwards run off.

Bismuth has a bright silvery lustre, tinged with red. It is highly crystalline and very brittle. Its sp. gr. is 9·8, and it melts at 270°. It is used in the preparation of several alloys, and its compounds are employed in medicine.

Certain alloys composed of bismuth (m.p. 270°), tin (m.p. 232°), and lead (m.p. 326°) melt at low temperatures, and are used for various purposes under the name of fusible alloys. *Rose's metal*, composed of bismuth (2 parts), tin (1 part), and lead (1 part), melts at 94°; an alloy (*Wood's metal*) of even lower melting-point (60·5°) may be prepared by mixing together bismuth (4 parts), tin (1 part), lead (2 parts), and cadmium (1 part).

Bismuth is converted into its trioxide when it is strongly heated in the air. It combines with the halogens, giving compounds of the type BiX_3, and is readily acted on by concentrated nitric acid, giving bismuth nitrate. It does not combine with hydrogen.

Bismuth nitrate, $Bi(NO_3)_3$, is obtained in colourless hydrated crystals when bismuth, or its oxide, hydroxide, or carbonate is treated with nitric acid and the solution is evaporated. The salt cannot be purified by recrystallisation from water, but may be recrystallised from dilute nitric acid; its solution in nitric acid gives, with a large volume of water, a colourless precipitate of a basic salt, owing to the occurrence of hydrolysis,

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2 \cdot NO_3 + 2HNO_3.$$

The nature of the basic salt depends on the conditions of the experiment; when the precipitate is well washed with water it has the above composition, and is used in medicine under the name of *bismuth oxy-nitrate* or *sub-nitrate*. The basic salt is reconverted into the normal salt, and passes into solution when it is treated with nitric acid.

Bismuth trichloride, $BiCl_3$, is obtained by heating bismuth in a stream of chlorine. It is a colourless crystalline substance, and boils at 435°. Like the nitrate, it is hydrolysed by water, giving a white insoluble basic salt, **bismuth oxychloride,**

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

This reaction, which is readily reversible, is employed in testing for bismuth.

Bismuth hydroxide, $Bi(OH)_3$, is obtained as a white flocculent precipitate when ammonium hydroxide or an alkali hydroxide is added to a solution of a bismuth salt; it is a basic hydroxide corresponding to the bismuth salts just described.

Bismuth trioxide, Bi_2O_3, prepared by heating the hydroxide or nitrate of bismuth, is a yellow basic oxide, and with strong acids it gives the bismuth salts.

Bismuth sulphide, Bi_2S_3, is obtained as an almost black precipitate when a solution of a bismuth salt, acidified with hydrochloric acid, is treated with hydrogen sulphide,

$$2BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl.$$

Unlike the sulphides of arsenic and of antimony it is not soluble in ammonium sulphide.

Bismuth is said to form several oxides in addition to the basic oxide, Bi_2O_3 Thus when bismuth hydroxide, suspended in a solution of potassium hydroxide, is treated with chlorine, it undergoes oxidation, and yields products to which the formulæ Bi_2O_4 and Bi_2O_5 have been given. On the other hand, when the suspension of the hydroxide is treated with stannous chloride the hydroxide is reduced to a black solid, which seems to have the composition BiO.

Vanadium, V, at. wt. 51·2, was first obtained by Roscoe. It forms five compounds with oxygen--namely, V_2O, VO, V_2O_3, VO_2, and V_2O_5. **Niobium,** Nb, and **tantalum,** Ta, are closely related to vanadium. Tantalum filaments are used in electric lamps.

THE RELATIONSHIP BETWEEN THE ELEMENTS OF THE NITROGEN FAMILY.

When the properties of the five elements, nitrogen, phosphorus, arsenic, antimony, and bismuth are compared, it is seen that although there is a great difference between, say, nitrogen and phosphorus, or phosphorus and arsenic, as regards physical properties, there is considerable similarity in chemical properties.

The five elements form corresponding compounds of the same type, and the properties of these corresponding compounds are on the whole very similar; for these reasons the elements are classed together in the 'nitrogen family.'

Now, just as in the case of the members of the halogen family, the relationship between the five elements of the nitrogen family is most clearly observed by arranging these elements in the order of their atomic weights; when this is done the dissimilarity between any two successive elements is seen to be the expression of a gradual and regular change.

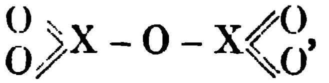
As an example of this change in physical properties the specific gravities may be noted; but it must at the same time be pointed out that in the case of some physical properties, such as melting-point, the change is by no means so regular:

	Nitrogen.	Phosphorus.	Arsenic.	Antimony.	Bismuth
At. wt.	14	31	75	120·2	208
Sp. gr.	1·0 (at $-252°$)	1·8 – 2·1	3·9 – 5·7	6·7	9·8

The relationship in chemical properties between the members of this family is clearly indicated by tabulating some of their more important compounds:

Molecular Formula.	Hydride.	Chlorides.		Oxides.	
N_2	NH_3	NCl_3(?)		N_2O_3	N_2O_5
P_4	PH_3	PCl_3	PCl_5	P_2O_3	P_2O_5
As_4	AsH_3	$AsCl_3$		As_2O_3	As_2O_5
Sb_2	SbH_3	$SbCl_3$	$SbCl_5$	Sb_2O_3	Sb_2O_5
Bi_2	—	$BiCl_3$		Bi_2O_3	Bi_2O_5

From the similarity in type in the case of any series of corresponding compounds it is clear that the five elements show the same valencies. In their hydrides and chlorides they are all *tervalent*, but some of them also form halogen compounds (PCl_5, AsF_5, $SbCl_5$) in which they are quinquevalent.

In their lower oxides of the type X_2O_3 they are also tervalent, as indicated in the formula $O = X - O - X = O$, but in their highest oxides, X_2O_5 or  $\begin{smallmatrix}O\\O\end{smallmatrix}\!\!>\!X - O - X\!<\!\!\begin{smallmatrix}O\\O\end{smallmatrix}$, they are quinquevalent.

In the case of any series of corresponding compounds there is a gradual change in passing from the derivatives of nitrogen to those of bismuth. The nature of this change may be summarised in the statement that those properties which characterise a non-metal gradually become less marked, while those pertaining to a metal gradually become more pronounced. Thus one of the respects in which non-metals as a class differ from metals is that the former give gaseous or readily volatile *hydrides*. In this family, four out of the five elements give rise to such hydrogen compounds; but the stability of these hydrides, as indicated by their heats of formation or by the temperatures at which they rapidly decompose, diminishes regularly in passing from ammonia to stibine; the solubility of the hydrides in water and the stability of their salts also diminish regularly, the compounds of arsenic and of antimony being only sparingly soluble and giving no stable salts..

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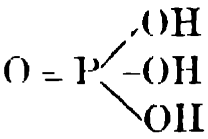
* The allotropic forms of phosphorus and those of arsenic have different specific gravities; hence the wide range given above. Except in the case of nitrogen, the values refer to ordinary temperatures.

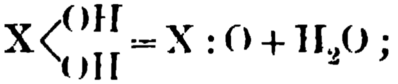
On turning to the chlorides and the oxides, the gradual weakening of the non-metallic character of the element is more distinctly noticeable. The trichlorides of nitrogen and of phosphorus undergo a non-reversible hydrolysis in aqueous solution; the trichlorides of the other three elements are also hydrolysed, but the changes are reversible, and increasingly so under similar conditions in passing from arsenic to bismuth. The lower oxides, which correspond with these chlorides, afford a similar illustration; those of nitrogen and of phosphorus have the properties of anhydrides; arsenious oxide is an anhydride, but may also act as a weak basic oxide towards strong acids; antimonious oxide shows acidic properties, but its basic character perhaps predominates; bismuth trioxide is distinctly a basic oxide.

The highest oxides, X_2O_5, except that of bismuth, are all anhydrides, but the acids derived from them become weaker in passing from nitric to metantimonic acid.

Although the general relationship between the members of this family is so clearly established by the illustrations given above, it must be again pointed out that in this, as in other families, individual elements show abnormal properties, and that judgment by analogy must not take the place of a knowledge of facts. In this family notable examples of such irregularities cannot fail to attract attention; the existence of the oxides N_2O and NO, the non-existence of the acid H_3NO_4, or of salts derived from it, and the fact that only phosphorus and antimony form pentachlorides are cases of this kind.

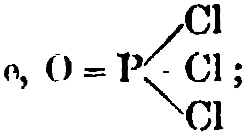
As regards the constitutions of the various compounds derived from the elements of this family, it may be observed that those of the nitrogen compounds may be taken as representative,* except of course in the case of the acids H_3XO_3 and H_3XO_4 and their derivatives.

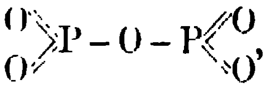
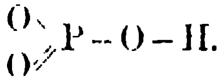
The structure of phosphoric acid is expressed by the formula  $\mathrm{O=P}\begin{array}{l}\diagup\mathrm{OH}\\-\mathrm{OH}\\\diagdown\mathrm{OH}\end{array}$; this expression is based on considerations such as the following: Phosphorus forms a pentachloride which is hydrolysed by water, giving H_3PO_4. When a chloride is hydrolysed the process always consists primarily in the displacement of univalent chlorine atoms by univalent hydroxyl-groups. In most cases this is clearly established by the fact that the number of hydroxyl-groups in the product of hydrolysis corresponds with the number of chlorine atoms which have been displaced. In cases where this is not so, the formation of the final product can always be accounted for by assuming the occurrence of a secondary reaction, in which the hydroxyl-groups, acting in pairs, give rise to water. One oxygen atom from each pair of hydroxyl-groups thus becomes combined by both its hooks or valencies to the element with which it remains united, as indicated by the expression,

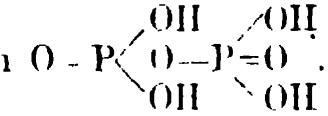


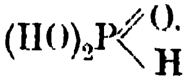
$$\mathrm{X}\begin{array}{l}\diagup\mathrm{OH}\\\diagdown\mathrm{OH}\end{array}=\mathrm{X:O}+\mathrm{H_2O};$$

the process, in fact, is a reversal of that which occurs when an oxide is transformed into the corresponding hydroxide (p. 468).

Now, these generalisations being applied to the hydrolysis of phosphorus pentachloride, the first change probably results in the formation of a compound, $PCl_3(OH)_2$, which loses the elements of water, giving phosphorus oxychloride,  $\mathrm{O=P}\begin{array}{l}\diagup\mathrm{Cl}\\-\mathrm{Cl}\\\diagdown\mathrm{Cl}\end{array}$; further hydrolysis then leads to the production of phosphoric acid, the molecules of which, therefore, doubtless have the structure $O \quad P(OH)_3$.

This view is confirmed by the fact that phosphoric acid is *tribasic*, because in hydroxy-acids all the displaceable hydrogen is contained in hydroxyl-groups (p. 492); also by a study of the relation between phosphoric acid, metaphosphoric acid, pyrophosphoric acid, and other compounds. Metaphosphoric acid is the first product of the action of water on the pentoxide; if the structure of this oxide is represented by the formula  $\begin{matrix}O\\O\end{matrix}\!\!>P-O-P\!\!<\!\!\begin{matrix}O\\O\end{matrix}$, then, since one molecule of the oxide gives two molecules of the hydroxide or acid, and the production of the latter probably occurs in the usual manner, the structure of the resulting compound would be  $\begin{matrix}O\\O\end{matrix}\!\!>P-O-H$.

Since metaphosphoric acid combines directly with water, giving phosphoric acid, and in this reaction the grouping $>P=O$ becomes $>P(OH)_2$, the above view of the constitution of phosphoric acid is confirmed. The fact that a *tetrabasic* acid, namely, pyrophosphoric acid, is formed from two molecules of phosphoric acid by the elimination of one molecule of water is also in accordance with the above structural formula, and the constitution of pyrophosphoric acid is written  $O-P\!\!<\!\!\begin{matrix}OH\\O-\overset{OH}{\underset{OH}{P}}=O\\OH\end{matrix}$.

Although phosphorous acid is a relatively simple compound, and its formation from phosphorus trichloride would seem to leave little room for doubt as to its constitution, it is not certain whether its structure is $P(OH)_3$ or  $(HO)_2P\!\!<\!\!\begin{matrix}O\\H\end{matrix}$. Towards basic hydroxides it behaves as a *di*-basic and not as a *tri*-basic acid, a fact which seems to show that the original product of the hydrolysis of PCl_3 undergoes a change in structure into the compound represented by the second of the above formulæ. Such a change in *structure* which occurs within the molecule of a compound is known as an *intramolecular* or *isomeric change.*

CHAPTER LV.

The Elements of the Carbon Family.

This family includes the very important element carbon (p. 113), which is classed with silicon, tin, and lead, and several other elements of comparatively rare occurrence. The compounds of carbon are so numerous and so different in general behaviour from those of other elements that it is convenient to consider them collectively in separate text-books.[*] At the same time there are certain carbon compounds, such as the oxides (pp. 62, 120),[†] carbonic acid and its salts [‡] (p. 271 *et seq.*), and a few other acids composed of carbon, hydrogen, and oxygen (p. 277 *et seq.*), which should be studied in a first-year course, and which, consequently, have been described in Part I.

In dealing, then, with the elements of the carbon family it is unnecessary to give here any further account of the compounds of carbon; a few of them are mentioned later, but only incidentally.

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[*] *Organic Chemistry*, Perkin and Kipping (W. & R. Chambers, 7s. 6d.).

[†] **Carbon suboxide**, C_3O_2, is formed when malonic acid is heated with phosphorus pentoxide,

$$CH_2(COOH)_2 + 2P_2O_5 = C_3O_2 + 4HPO_3.$$

It is a poisonous, disagreeably smelling gas, which decomposes at ordinary temperatures with separation of carbon; when treated with water it gives malonic acid.

[‡] **Percarbonic acid**, $HO \cdot CO \cdot O \cdot O \cdot CO \cdot OH$, is obtained in the form of a salt by the electrolysis of solutions of the acid alkali carbonates (compare persulphuric acid, p. 495). The free acid is not known.

SILICON, Si;* AT. WT. 28·3.

Silicon, next to oxygen, is the most abundant of all elements, and its oxide, silica, is the most important component or constituent of igneous or primary rocks (p. 290). The free oxide occurs in the pure crystalline state as colourless quartz or rock-crystal; coloured, slightly impure varieties of quartz are topaz (brown) and amethyst (violet). In a partly amorphous condition, often coloured by various metallic oxides, and sometimes containing combined water, silica is also found in the form of *agate*, *opal*, *jasper*, *chalcedony*, *flint*, &c. Most rock material, moreover, consists of mixtures of various silicates (pp. 290-292, 609).†

From sea sand, or any other impure form of silica, the element silicon may be obtained by first preparing pure amorphous silica in the manner already described (p. 293), and then reducing this oxide with magnesium (p. 294). The latter reaction is often a vigorous one, even when sand is used, and when very finely divided silica is employed a most dangerous explosion may occur; for this reason the *dry* mixture of silica and magnesium should be spread on an iron plate in a layer about half-an-inch thick, and heated cautiously at the outside in order to start the reaction. Excess of magnesium being used, the product consists of a mixture of silicon and **magnesium silicide,** Mg_2Si, and when it is warmed with dilute hydrochloric acid (p. 294) the silicide is decomposed, giving silicon hydride, a gas which is spontaneously inflammable in the air (p. 578).

The *amorphous* silicon, which is thus obtained in an impure state as a brown powder, dissolves in melted zinc, and when the solution cools *crystals* of silicon are formed; these may be isolated by dissolving away the zinc with dilute sulphuric acid.

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* The molecular formula of the element is unknown.

† Although silicon is such an inert element at ordinary temperatures, it does not occur in the free state. Like all those elements which give rise to stable, strongly exothermic oxides, the silicon present in the cooling mass of the earth doubtless combined with oxygen before the temperature had fallen sufficiently for the oxides of most of the other elements to be formed, and the silica thus produced has never since been decomposed. Elements which occur in the free state are those the oxides of which are relatively easily decomposed.

Crystallised silicon is a black, lustrous substance of sp. gr. 2·5; it is extremely inert, but it combines with chlorine when it is heated in this gas, and it is also attacked slowly by a boiling concentrated solution of potassium or sodium hydroxide,

$$Si + 4NaOH = Na_4SiO_4 + 2H_2.$$

The sodium orthosilicate thus formed probably undergoes hydrolysis and gives sodium metasilicate,

$$Na_4SiO_4 + H_2O = Na_2SiO_3 + 2NaOH.$$

Crystalline silicon is also attacked slowly by hydrofluoric acid, in presence of nitric acid, which oxidises the nascent hydrogen (compare p. 340),

$$Si + 4HF = SiF_4 + 4H.$$

Amorphous silicon is rather more readily attacked than the crystalline element; thus amorphous silicon burns to silica when it is heated strongly in the air, whereas the crystalline variety does not.

Silicon hydride or **silicane,** SiH_4, is formed in relatively very small quantities when silicon is heated with hydrogen at the temperature of the electric arc. It is obtained mixed with hydrogen and other hydrides of silicon (Si_2H_6, Si_2H_4) when crude magnesium silicide (which, as a rule, contains free magnesium) is warmed with dilute hydrochloric acid,

$$Mg_2Si + 4HCl = SiH_4 + MgCl_2.$$

The mixture of gases is spontaneously inflammable, probably owing to the presence of the hydride Si_2H_4, but pure silicane is not. Silicane is decomposed into its elements when it is passed through a red-hot glass tube.

Silicon tetrafluoride, SiF_4, a colourless gas, is formed when silica or any silicate is treated with hydrofluoric acid

(p. 400); but as it is decomposed by water no gas is evolved unless the hydrofluoric acid contains a relatively small quantity of water. For this reason silicon tetrafluoride is best prepared by generating (anhydrous) hydrogen fluoride in presence of silica; this is done by heating a mixture of calcium fluoride (p. 401), sulphuric acid, and sand,

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Silicon tetrafluoride fumes in the air and is decomposed by water, giving a gelatinous precipitate of *ortho-* or *meta-silicic acid* and a solution of **hydrofluosilicic acid,**

$$3SiF_4 + 4H_2O = H_4SiO_4$$
$$(\text{or } H_2SiO_3 + H_2O) + 2H_2SiF_6.$$

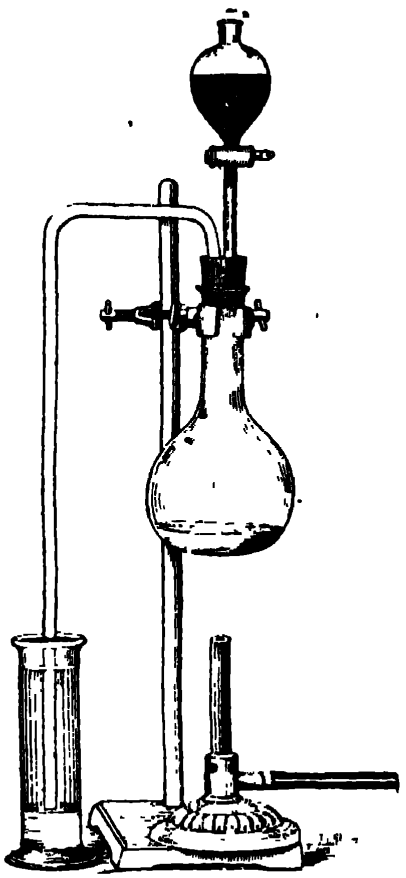

Fig. 109.

In preparing hydrofluosilicic acid by this method, the end of the delivery-tube from which the silicon tetrafluoride escapes is dipped under mercury (fig. 109), and the water is then poured on to the mercury. Mercury *must* be used to prevent the stoppage of the delivery-tube by the gelatinous metasilicic acid.

Hydrofluosilicic acid, H_2SiF_6, is only known in aqueous solution and in the form of its salts; it is a strong dibasic acid. When its solution is evaporated the acid decomposes, silicon tetrafluoride volatilises, and a solution of hydrogen fluoride remains; on continued evaporation (in a platinum vessel) no residue is left. The salts of the acid are decomposed in a similar manner when they are strongly heated,

$$K_2SiF_6 = 2KF + SiF_4.$$

Potassium fluosilicate is only very sparingly soluble in water. Since hydrofluosilicic acid is stable in aqueous solution, and its solution does not act on silica, a solution of hydrofluosilicic acid cannot contain either HF or SiF_4; the acid, therefore, is not a mixture of $2HF$ and SiF_4, but a compound formed from these two substances.

Silicon tetrachloride, $SiCl_4$, may be obtained by passing *dry* chlorine over a *dry* heated mixture of silica and charcoal,*

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO;$$

but as a very high temperature is required for this reaction, a more convenient laboratory method is to heat either amorphous silicon, or some cast-iron which is rich in silicon, in a stream of dry chlorine. The tetrachloride is collected in a well-cooled receiver; it is a liquid boiling at 59°.†

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* Neither silica nor charcoal *alone* is acted on by chlorine, and silica is not acted on by carbon at the temperatures employed in this experiment (compare p. 512).

† The relation between the equivalent and the atomic weight of silicon is based principally on determinations of the vapour density of silicon tetrachloride and other volatile silicon compounds, and not on an application of the law of Dulong and Petit (p. 199), to which silicon may be said to form an exception. Thus the specific heat of crystalline silicon is 0·17 at 22°, which would give to its atomic heat a value $0·17 \times 28·3 = 4·8$, if the atomic weight is 28·3.

Several other elements form 'exceptions' to the law of Dulong and Petit, notably *carbon* and *boron*, and to a less extent *sulphur* and *phosphorus*, inasmuch as, their specific heats being taken at ordinary temperatures, the values for their atomic heats are considerably below the average (or constant) value, 6·4. The specific heat, however, varies very greatly with the temperature at which it is determined, and, as shown by the following data, the atomic heats of silicon, carbon, and boron all approximate to the average value when their specific heats at *high temperatures* are taken instead of those at low temperatures:

	Specific Heat	Temperature at which determined	Atomic Heat.
Silicon (crystallised) .	0·1360	−40°	3·8
" " .	0·2029	232°	5·7
Diamond . . .	0·1128	11°	1·3
" . . .	0·4589	985°	5·5
Graphite . . .	0·1990	61°	2·4
" . . .	0·4670	978°	5·6
Boron . . .	0·1915	−40°	2·1
" . . .	0·3663	233°	4·3

Since it is impossible to say at what temperatures the specific heats of the elements should be taken in order to obtain comparable values, the

Silicon tetrachloride fumes strongly in the air and is violently hydrolysed by water, giving hydrochloric acid and a gelatinous precipitate of ortho (or meta) silicic acid,

$$SiCl_4 + 4H_2O = 4HCl + H_4SiO_4 \text{ (or } H_2SiO_3 + H_2O).$$

Silicon chloroform, $SiHCl_3$, is obtained as a volatile liquid (b.p. 34°) when dry hydrogen chloride is passed over heated amorphous silicon; it is hydrolysed by water, and the *silico-orthoformic acid*, $SiH(OH)_3$, which is probably the initial product, immediately passes into the *anhydride* $(HSiO)_2O$, derived from *silicoformic acid*, $HSiO{\cdot}OH$.

Silicon forms compounds with carbon, nitrogen, and many other elements at the temperature of the electric furnace. The carbon compound, **silicon carbide,** SiC, generally known as *carborundum*, is prepared on the large scale by heating sand with coke and sawdust at about 1950°, a little sodium chloride being added as a flux. The product is a brown or black infusible crystalline substance which resists the action of nearly every substance except fused alkali hydroxides. It is almost as hard as the diamond (which may be polished with carborundum), and it is largely used as an abrasive in cutting and polishing marble, in bevelling plate-glass, in sharpening tools, and in many other operations.

Silicon dioxide or **silica,** SiO_2, has already been described (pp. 292 and above). It is not acted on by any acid except hydrofluoric acid, but it is converted into sodium metasilicate when it is fused with sodium carbonate or when it is heated with a concentrated solution of sodium hydroxide; precipitated amorphous silica undergoes these changes far more rapidly than does the crystalline variety.

With the aid of the electric furnace, quartz is now melted and made into basins, tubes, &c., for use in chemical operations—as, for example, in the concentration of 'chamber acid.' Such apparatus has one great advantage over glass—namely, that it does not crack when it is suddenly heated or cooled.

'abnormal' behaviour of silicon, carbon, boron, &c., does not detract from the importance of Dulong and Petit's law, and does not throw any doubt on the accepted values for the atomic weights of these elements.

When a cold dilute aqueous solution of sodium silicate is poured into excess of dilute hydrochloric acid, the resulting solution contains a '*soluble*' colloidal acid (p. 327), which is possibly *orthosilicic acid*, H_4SiO_4,*

$$Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl.$$

No precipitate is produced until the solution is heated, but on boiling for some time *most* of the dissolved acid separates as a gelatinous solid, which may be called metasilicic acid; the whole of the soluble silicic acid, however, is not converted into this insoluble metasilicic acid unless the solution is evaporated to dryness and the residue is then heated at about 115°. The gelatinous precipitate is not constant in composition; when heated it is completely converted into amorphous silica.

The only *soluble* silicates are those of the alkali metals, and these compounds are formed in the manner described above; *sodium silicate* is a vitreous substance (soluble glass or water-glass) used in coating wood, &c., in order to render the material fireproof; also as a cement for stone and plaster work.

The soluble alkali silicates are hydrolysed by water and cannot be recrystallised, and the composition of any product depends on the method of preparation; thus commercial water-glass has approximately the composition $Na_2Si_4O_9$, or $Na_2SiO_3, 3SiO_2$, and is often only partially soluble in water.

The *molecular formula* of silica is not known, as its vapour density cannot be determined, nor its molecular weight in solution. Judged by indirect evidence, its molecular weight must be very large. In the case of similar elements, their corresponding compounds generally show a fairly regular difference in boiling-point, or have boiling-points of about the same order. Thus carbon tetrachloride, CCl_4, boils at 76°; silicon tetrachloride, $SiCl_4$, at 59°; chloroform,

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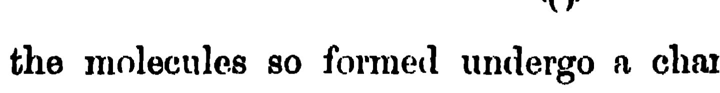
* **Orthosilicic acid has not been obtained in a pure state, nor has sodium orthosilicate, and it is not known whether the 'soluble' or colloidal acid is the ortho- or the meta-acid.**

$CHCl_3$, boils at 61·5°; silicon chloroform, $SiHCl_3$, at 34°; carbon tetrafluoride, CF_4, and silicon tetrafluoride, SiF_4, are both gaseous at ordinary temperatures and pressures. Now, since carbon dioxide boils (sublimes) at $-79°$ (p. 163), whereas silica only volatilises at the highest temperatures of the electric furnace, it is concluded that the incomparably higher boiling-point of silica is due to its great molecular complexity; that is to say, it is thought that the molecular formula of silica is probably $(SiO_2)_n$, where n is some fairly large whole number.

When identical molecules associate or combine directly, thus forming more complex molecules of the same empirical formula as the original substance, the product is often called a *polymeride* of the simpler substance, and the change which the latter undergoes is termed **polymerisation.** The phenomenon of polymerisation is closely related to that of association (p. 384), and it is often impossible to distinguish between them; but as a general rule it may be said that the change is called polymerisation when there is some evidence that the molecules of the simple substance undergo a change in *structure.*

Ordinary silica is doubtless a polymeride or a polymeric form of the simple oxide, SiO_2; but there are probably many varieties of silica, differing from one another in molecular formula.

The nature of the union between the molecules of the oxide, SiO_2, in its polymeric forms is not known, but it may be that combination occurs as indicated in the following scheme:



$$\mathrm{O:Si:O+O:Si:O\longrightarrow O:Si{<}\genfrac{}{}{0pt}{}{O}{O}{>}Si:O},$$

and that the molecules so formed undergo a change of the same kind, which is possibly repeated many times.

A comparison of the properties of metasilicic acid with those of carbonic acid seems to show that the former, like its anhydride, also consists of highly complex molecules.

Polysilicic Acids.—In addition to the different polymeric forms of metasilicic acid which probably exist, many other acids derived from the anhydride, SiO_2, are known in the form of their salts; these acids are named the **polysilicic acids,** and many of their salts, like those of ortho- and meta-silicic acids, are important components of the earth's crust.

Just as the hydroxide $P(OH)_5$ gives rise to ortho-, pyro-, and meta-phosphoric acid (p. 571), so also *orthosilicic acid*, $Si(OH)_4$, gives rise not only to metasilicic acid but to various other acids having compositions expressed by the formula $nSi(OH)_4 - mH_2O$. These acids are distinguished as *disilicic acid, trisilicic acid*, and so on, according to the number of silicon atoms contained in their empirical formulæ. *Orthoclase* (p. 290), for example, may be regarded as a potassium aluminium salt of a trisilicic acid, since $3Si(OH)_4 - 4H_2O$ would give an acid $H_4Si_3O_8$, the potassium aluminium salt of which would have the composition of orthoclase—namely, $KAlSi_3O_8$. Mica (p. 291) may be regarded as a mixture of the silicates $KAlSiO_4$ and $2HAlSiO_4$, derived from orthosilicic acid. The compositions of such minerals are often expressed somewhat differently (p. 609). The great variety of rock materials is thus due to the occurrence of numerous salts of various silicic acids, and these salts may be not only mixed together, but may form isomorphous mixtures or solid solutions with one another (p. 323).

Germanium, Ge, at. wt. 72·5, forms a connecting link between silicon and tin, and its properties are such as would be expected from its position in the periodic system. It gives rise to two oxides, namely, **germanous oxide,** GeO, and **germanic oxide,** GeO_2; but even the lower oxide is only feebly basic, and germanium itself is insoluble in hydrochloric acid. It does not form a hydride, but it gives a **tetrachloride,** $GeCl_4$, which is hydrolysed by water. Germanium is a very rare element, and is of interest chiefly on account of its existence having been predicted (p. 726).

TIN, Sn; AT. WT. 119.

Although manganese and chromium are metals, they are seldom seen, and are at present little used except in the form of alloys. Bismuth, although a fairly common metal, is also of limited usefulness. The metal tin, therefore, is the first case to be considered of a metal which is prepared in very large quantities (about 95,000 tons per annum), and is in daily use. For this reason one of the various methods of extracting the metal from its 'ore' is described in some detail, as an illustration of such large-scale metallurgical operations.

Tin is not found in the native state. It occurs almost entirely in the form of the dioxide, SnO_2, in the mineral *tin-stone* or *cassiterite*, which is mined in large quantities in the Malay Peninsula and also occurs in many other parts of the world; the tin-mines of Cornwall, for example, have been worked since very early times.

Cassiterite is of a dark-gray colour owing to the presence of black sulphides; it generally contains arsenical pyrites (p. 552), copper pyrites, and other minerals, and its specific gravity is about 6·5.

The reduction of the dioxide to the metal is easily accomplished by heating the cassiterite with some carbonaceous material such as anthracite (p. 118),

$$SnO_2 + 2C = Sn + 2CO;$$

but before this is done it is necessary to get rid of the combined arsenic and sulphur in the ore. It is also necessary so to arrange matters that the earthy impurities (*gangue*), consisting in this case principally of silica, are transformed into some product which can be *melted* and then run off, or raked off, the melted metal; this fusible product is known as a **slag**, and the material which is added in order to convert the earthy impurities into a fusible slag is known as a **flux**.

These results are accomplished in the following manner: After the ore has been sorted and crushed, and freed from lighter earthy matter by washing it with water (p. 29), it is first roasted (p. 229) in a reverberatory furnace (fig. 110) in order to *oxidise* the sulphides and arsenides of iron and copper. The arsenical pyrites is thus converted into sulphur dioxide, arsenious anhydride, and ferric oxide, and the copper pyrites into sulphur dioxide, copper oxide, and copper sulphate. The furnace gases are passed through long flues or condensing chambers in which the arsenious anhydride (p. 555) is deposited. The ore is afterwards washed with water to free it from copper sulphate, and with dilute hydrochloric or sulphuric acid to free it from copper oxide.

The prepared ore, which consists essentially of tin dioxide, silica, and ferric oxide, is mixed with 15 to 20 per cent. of anthracite and a little slaked lime, the mixture is damped with water (to lay the dust), and placed in a reverberatory furnace, in which it is gradually heated to a suitable temperature. The tin dioxide is then reduced, while the silica combines with the oxides of iron and of calcium to form a fusible *slag*. The contents of the furnace finally separate into two layers; after the molten slag is raked off the surface of the metal, the tin is run out through a tap-hole placed at the lowest part of the hearth or bed of the furnace.

A reverberatory furnace such as is used in 'smelting' tin ores and in many similar metallurgical operations is shown below (fig. 110). The bed (*a*) of the furnace, which may be from 5 to 12 feet long, and from 3½ to 8 feet broad, consists of fire-clay supported on iron bars. The charge is introduced through the door (*b*), and the slag is withdrawn through the door (*c*). The necessary raking and stirring of the charge are also carried on through these doors. The contents of the furnace are heated from above; the flame from the fire (*d*) passes over the fire-bridge (*e*), and is deflected from the low roof of the furnace, the necessary draught being produced by the chimney (*f*). The tin is run off through the tap-hole, which is meanwhile plugged with clay, and is then cast into moulds.

In order to purify the metal, the 'ingots' are gradually heated on the sloping hearth of a reverberatory furnace, whereupon the tin (which has a low melting-point) liquefies and runs away into a receiver (heated by a fire below), leaving a less fusible mixture of iron, arsenic, and other impurities. This process is called *liquation.*

The metal is then skimmed to remove oxides (dross), and a bundle of green logs, fastened to an iron bar, is pushed under the surface. The escape of steam and gases from the wood (as a result of its destructive distillation, p. 114) causes a 'boiling,' and the metal is thus brought into contact with the air, whereby most of the impurities are oxidised. Instead of this process, the molten metal may be taken up in ladles and poured into another vessel in a thin stream ('tossing'). In either case the dross which is thus formed is finally removed, and after the metal is allowed to settle for some time it is ladled into moulds. The upper portions consist of almost pure tin; any copper and iron which may be present collect in the lower portions, and the latter are again refined.

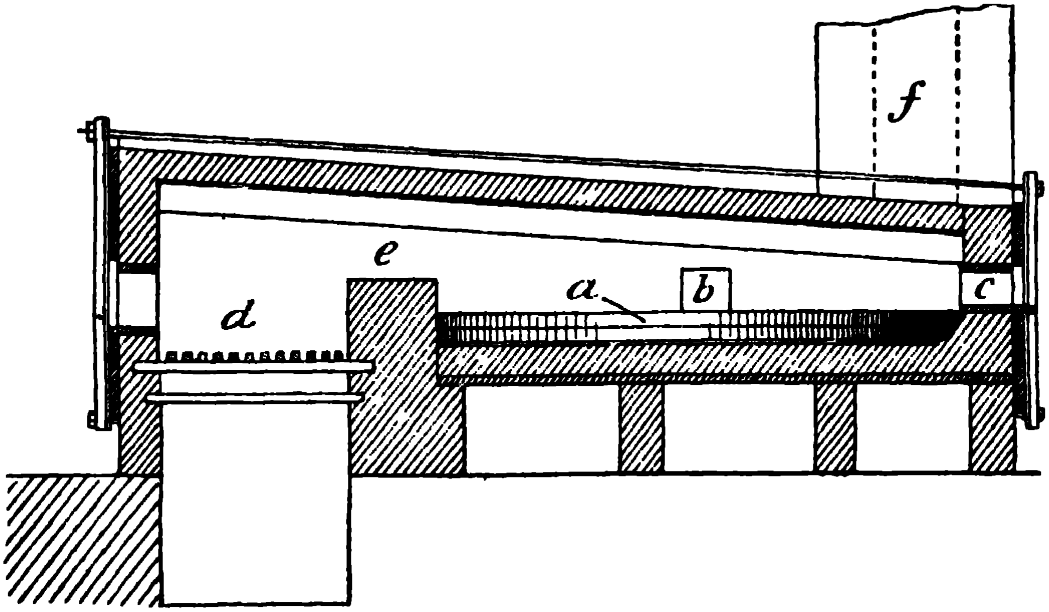


Fig. 110.

Commercial tin of good quality contains only 0·1 to 0·2 per cent. of impurity, which consists principally of antimony, lead, and iron.

Tin is a highly lustrous, silvery metal of sp gr. about 7·3, and harder than lead, but softer than other common metals. It is easily obtained in distinct crystals; if, for example, a rod of zinc is placed in a solution of stannous chloride, the tin which is displaced separates on the zinc rod in a crystalline form,

$$SnCl_2 + Zn = Sn + ZnCl_2.$$

Rods of the metal when bent emit a low grating sound, known as the 'cry of tin,' which is due to the crystal faces grinding against one another.

In spite of its crystalline character, tin is very *malleable* at ordinary temperatures—that is to say, it may be rolled or beaten into thin sheets (tin-foil); on the other hand, just below its melting-point it is brittle, and may then be powdered. It melts at about 232° and boils at a white-heat.

Tin may slowly change and become gray and brittle when it is exposed to a low temperature for a long time, owing to its transformation into a more stable allotropic form; the occurrence of this change is known as the 'tin pest.'

Tin is used for making still-heads, condensers, and other vessels for domestic, laboratory, or manufacturing purposes; in the form of tin-foil it is employed in making mirrors, in lining boxes, in packing various articles, &c. Perhaps its most important applications, however, are for coating other metals, especially iron and copper.

In manufacturing *tin-plate*, the material so widely used in making 'tins' for preserved foods, &c., thin sheet-iron, very carefully cleaned, is dipped into molten tin. The coating of tin prevents the rusting of the iron

When a piece of tin-plate is placed for a few moments in a suitable solution, such as a mixture of hydrochloric acid (2 parts), nitric acid (1 part), and water (3 parts), and is then washed with water, the surface is etched and the crystals of tin are often very clearly seen, because the different faces of the crystals are corroded to different extents.

Alloys of tin and lead, containing from 66 to 33 per cent. of tin, form plumber's *solder* of various qualities; an alloy of 3 parts of tin to 1 part of lead is known as *pewter*. *Britannia metal*, a silver-white alloy used in making spoons, &c., consists of tin (9 parts) and antimony (1 part), sometimes with a little zinc and traces of copper. Bronze and other important alloys of tin and copper are mentioned later (p. 654).

Tin does not oxidise to any appreciable extent even in moist air at ordinary temperatures; but when strongly heated it burns brightly and is rapidly converted into the dioxide. It is rather easily attacked by hot concentrated hydrochloric acid, giving stannous chloride, with liberation of hydrogen; by hot concentrated sulphuric acid, giving stannous sulphate, sulphur dioxide, and water; and by concentrated nitric acid, giving insoluble metastannic acid (p. 592) and reduction products of nitric acid (p. 530). When boiled with sodium hydroxide it gives hydrogen and a solution of sodium metastannate,

$$Sn + 2NaOH + H_2O = 2H_2 + Na_2SnO_3.$$

Stannous chloride, $SnCl_2$, is the starting-point in the preparation of many of the tin compounds, and is obtained in hydrated crystals, $SnCl_2, 2H_2O$, when the metal is heated with concentrated hydrochloric acid, and the solution is afterwards concentrated.

This salt is readily soluble in water, but is hydrolysed to a slight extent, giving an insoluble basic salt, $SnCl(OH)$; on a little hydrochloric acid being added, the reaction is reversed and the solution becomes clear.

On exposure to the air such solutions undergo oxidation and stannic chloride is formed; as this change occurs in presence of hydrochloric acid, produced by the hydrolysis of the stannous chloride, it may be expressed by the equation,

$$2SnCl_2 + 4HCl + O_2 = 2SnCl_4 + 2H_2O.$$

In consequence of the readiness with which stannous chloride is oxidised it is used in the laboratory as a reducing agent. Thus it reduces the higher chlorides of iron, copper, and mercury to the lower chlorides,

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$
$$2CuCl_2 + SnCl_2 = 2CuCl + SnCl_4,$$

and in the case of mercury it also reduces the lower chloride to the metal,

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4.$$

The reactions expressed by the last two equations are used in testing for 'mercury' and for 'tin' in qualitative analysis.

Stannous chloride is used as a mordant under the name of '*tin salt.*'

Stannous hydroxide, $Sn(OH)_2$, is obtained as a colourless precipitate on a solution of an alkali hydroxide or an alkali carbonate* being added to a solution of the chloride. It gives, with acids, the corresponding stannous salts, but towards the alkali hydroxides it acts as a weak acid, and gives soluble *stannites*,

$$Sn(OH)_2 + NaOH = Sn(OH)ONa + H_2O$$
or
$$Sn(OH)_2 + 2NaOH = Sn(ONa)_2 + 2H_2O.$$

The stannites are unstable and decompose when their solutions are heated, giving a metastannate and a deposit of tin,

$$2Sn(OH)ONa = Na_2SnO_3 + H_2O + Sn.$$

Stannous oxide, SnO, a brown powder, prepared by heating the hydroxide out of contact with oxygen, burns in the air, giving stannic oxide.

Stannic chloride, $SnCl_4$, is prepared by passing a stream of dry chlorine over granulated tin; an apparatus such as that shown in fig. 107, p. 544, may be used. The product is a colourless fuming liquid, which boils at 114°, and is easily purified by distillation. When mixed with a small proportion of water it gives hydrated crystals, $SnCl_4, 3H_2O$ (*butter of tin*), which are soluble in water, but in time the salt undergoes hydrolysis and soluble stannic acid is formed,*

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* Stannous carbonate is not obtained, doubtless because it undergoes hydrolysis.

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl.$$

When such solutions are boiled or treated with ammonium hydroxide the soluble stannic acid is converted into an insoluble (meta) stannic acid, the composition of which may be represented by the formula H_2SnO_3; this substance dissolves chemically in hydrochloric acid, forming stannic chloride, and in alkalis, giving (meta) stannates, such as Na_2SnO_3.

Ammonium stannichloride, $SnCl_4, 2NH_4Cl$ or $(NH_4)_2SnCl_6$, is obtained by mixing stannic chloride and ammonium chloride in aqueous solution, and then concentrating the solution; similar compounds are formed from stannic chloride and the chlorides of some of the alkali metals.

The compounds thus obtained are doubtless produced from their constituents by chemical change, and are not mere double salts (p. 322) or solid solutions, but salts of an acid, H_2SnCl_6.

Many cases are known in which two salts unite directly, giving a compound which does not show some of, or all, the reactions of *one* of its constituent metals, and when such compounds undergo electrolysis this particular metal is contained in the negative ions, while the other metal forms the positive ions. In such cases it must be concluded that the two salts have undergone chemical change and have united to form a more complex substance. Salts of this kind, for want of a better term, are spoken of as *complex salts*, and the acids corresponding with them as *complex acids*.

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* It is probable that this hydrolysis occurs in stages, soluble compounds such as $SnCl_3 \cdot OH$, $SnCl_2(OH)_2$, being first formed.

It is often very difficult to decide whether a given substance should be regarded as a double salt or as a complex salt, as they grade into one another, and many complex salts are more or less decomposed in aqueous solution. Some complex salts, however, such as the complex cyanides (pp. 705, 708), are very stable.

Complex salts are also formed in other ways; as, for example, by the combination of a salt with the halide of a non-metal, as in the case of the fluosilicates (p. 579).

Stannic oxide, SnO_2, may be obtained by treating tin with excess of concentrated nitric acid until all the metal has been changed. The product is then washed with water, and afterwards ignited; while hot it is yellow, but it becomes colourless when cooled, without undergoing a change in composition.

This preparation is only very slowly changed into a soluble chloride by concentrated hydrochloric acid, but when fused with alkali hydroxides it gives metastannates which are soluble in water.

The original product of the action of nitric acid on tin is probably metastannic acid, H_2SnO_3; but this preparation is not readily soluble in sodium hydroxide, like that precipitated from a solution of stannic chloride on the addition of ammonium hydroxide; the cause of this difference is unknown, but it may be that the acids are different polymerides (p. 583) of H_2SnO_3.

The sulphides of tin correspond with the oxides, and may be precipitated by passing hydrogen sulphide through solutions of stannous and stannic chlorides respectively.

Stannous sulphide, SnS, is dark brown, and **stannic sulphide**, SnS_2, is yellow.

They are both readily acted on by a solution of *yellow* ammonium sulphide (p. 567), and are *both* converted into soluble ammonium thiostannate,

$$SnS + (NH_4)_2S,S = (NH_4)_2SnS_3$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

On hydrochloric acid being added to solutions of this salt stann*ic* sulphide is precipitated. Stann*ous* sulphide is not acted on by colourless ammonium sulphide (p. 567), but concentrated hydrochloric acid converts both sulphides into chlorides.

LEAD, Pb; AT. WT. 207·1.

Lead is very rarely found in the native state, and its principal ore is a black, lustrous, crystalline mineral known as *galena*, which consists of lead sulphide, PbS, but generally contains a very small proportion of silver sulphide, Ag_2S.

Cerussite, $PbCO_3$, *anglesite*, $PbSO_4$, and *crocoisite*, $PbCrO_4$, are other ores of lead.

The method employed in obtaining the metal from galena depends on the fact that when lead sulphide is strongly heated with lead oxide or with lead sulphate all these compounds are reduced and sulphur dioxide is evolved,

$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

The process, therefore, consists in oxidising *some* of the sulphide to oxide and sulphate at a relatively low temperature,

$$2PbS + 3O_2 = 2PbO + 2SO_2$$
$$PbS + 2O_2 = PbSO_4,$$

and then melting the whole mass in order to bring about reduction. The operations are carried out in a reverberatory furnace (fig. 110, p. 587), and the molten metal is finally run off into an iron 'kettle;' here it is well stirred with coal slack (coal dross) and some live coals to reduce any remaining oxides, and after the slack is skimmed off, the metal is cast into moulds. This product is impure, and contains variable quantities of antimony, copper, silver, &c., which render it hard. It may be refined by keeping it melted and stirring it in the air, when most of the impurities are oxidised and are then skimmed off as a 'dross;' it is further refined during the processes which are used in extracting silver from it (p. 594).

When galena contains earthy matter (silica) and other impurities, its reduction by the above process is unsatisfactory, owing to the formation of lead silicate; in such cases the ore is strongly heated with iron and coke and a flux (p. 585) in a small blast-furnace. The lead sulphide is then reduced by the iron,

$$PbS + Fe = Pb + FeS,$$

and the sulphide of iron thus formed gives, together with some sulphide of lead, a fusible product (matte); the lead and the matte are tapped out together, and when the latter has solidified at the surface of the molten metal it is removed. The silica combines with ferrous oxide (produced from ferric oxide which is added as a flux) to form a fusible slag, which is drawn off the surface of the matte before the furnace is tapped.

For the reduction of oxides of lead a process similar to that just described is employed, but the reduction is then brought about by the carbon of the fuel, or by the carbon monoxide formed from it (p. 288); iron is not added, but is produced in the furnace from oxides of iron which are added as a flux, and therefore any sulphide of lead present in the furnace charge is also reduced.

The three processes described above are known as the air reduction, the iron reduction or precipitation, and the carbon reduction process respectively.

The smoke and fumes from the furnaces in which lead ores are treated contain oxide of lead and many other substances, and are led into chambers or flues in which the solid matter is deposited.

Extraction of Silver from Crude Lead.—Although the quantity of silver contained in crude lead may be very small (say 0·15 per cent.), it is possible to extract this silver profitably, and at the same time to purify the lead, even when the quantity of silver amounts to less than 0·01 per cent. (that is, less than about 3½ oz. per ton).

Processes based on two different principles are used for this purpose.

Parke's process depends on the fact that when molten argentiferous lead is thoroughly stirred with a small proportion (say 1·5 per cent.) of zinc, and the metals are then left to cool slowly, the zinc separates from the lead, rises to the surface, and carries with it most of the silver which was contained in the lead; the zinc alloy, which solidifies before the lead, may be then removed and the process repeated if necessary with a fresh quantity of zinc.

The zinc alloy, which is mixed with a large proportion of lead, and with small quantities of other metals originally present in the crude lead, is first liquated (p. 587) and then strongly heated in plumbago crucibles; the zinc which distils off is condensed. The remaining alloy of lead and silver is finally submitted to cupellation (p. 596) in order to obtain the silver.

After treatment with zinc the lead is practically free from silver, but it now contains a small proportion (say 0·75 per cent.) of zinc, as this metal does not separate completely from the molten lead, this impurity is got rid of by melting the lead and blowing air over the surface. The zinc and some lead are thus oxidised, and the scum or dross is scraped from the molten metal, the process being continued until the dross consists of pure lead oxide. The pure 'soft' lead is then run into moulds.

Pattinson's process depends on the fact that when molten argentiferous lead cools slowly, crystals of pure lead are first deposited from the liquid mixture; by separating these crystals from the argentiferous mother liquor as completely as is practicable, one portion of the metal is obtained much richer, another much poorer, in silver than the original argentiferous lead. Each of these portions may now be treated in the same way as was the original material, and by repeating these processes in a systematic manner it is possible to obtain (*a*) a very rich argentiferous lead, and (*b*) lead practically free from silver. During these operations the other impurities in the lead are oxidised and removed as dross, so that the metal finally obtained is almost chemically pure.

In carrying out Pattinson's process the crude lead is melted in large iron pans (holding about 9 tons) which are heated by a fire below; the scum or dross of oxides is scraped off, and the metal is then cooled if necessary by throwing water on the surface.

When crystallisation commences the metal is kept well stirred, and, as crystals form, they are removed with long perforated ladles; this process is continued until about $\frac{2}{3}$ of the whole has been removed. The original sample having contained, say, 0·07 per cent. of silver (25 oz. per ton), the enriched $\frac{1}{3}$ may now contain, say, 0·13 per cent. (47 oz. per ton) and the impoverished $\frac{2}{3}$ only 0·04 per cent. (14 oz. per ton). If now the enriched portion, mixed with one or more similar charges from other operations, is again treated, the proportion of silver in the enriched material may then reach, say, 0·2 per cent. Similarly, by a second treatment of the impoverished lead which contains 0·04 per cent. of silver, the quantity of the latter may be reduced to, say, 0·03 per cent. These processes having been repeated several times, the final products are *market-lead*, which contains only about 0·0015 per cent. of silver, and argentiferous lead, which may contain as much as 1 per cent. (360 oz. per ton) of silver.

The rich argentiferous lead is now submitted to *cupellation.* It is melted in a furnace and an air-blast is played on the surface of the metal. The lead is thus oxidised and the lead oxide (litharge) which is formed is removed; this operation is continued until the whole of the lead has been oxidised, and there then remains a bright mass of silver. The lead oxide produced in this process may be used, as such, or reduced again to metal.

The bed of the cupel-furnace is lined with bone-ash (p. 535), which is very porous. Most of the molten litharge is blown off the surface of the metal by the air-blast; the rest is absorbed by the porous furnace-bed.

Lead is a soft metal of sp. gr. 11·3; it has a somewhat bluish-gray, silvery lustre, but it soon tarnishes on exposure to the air. It melts at 326° and crystallises readily. Thus it is deposited in crystals when a piece of zinc is placed in a solution of some lead salt, such as lead acetate (p. 279),

$$Pb(C_2H_3O_2)_2 + Zn = Pb + Zn(C_2H_3O_2)_2.$$

It is malleable, and may be rolled or beaten into foil, and two clean surfaces may be welded together; when warm it may be forced through dies and formed into pipes, but it becomes brittle just below its melting-point. Its physical properties are very considerably modified even by small quantities of other elements; a little (0·5 per cent.) arsenic, for example, makes it very much harder and less malleable.

Lead is used principally in the manufacture of water- and gas-pipes, and of sheets which are employed for roofing purposes, for making cisterns, pans, &c., and for the construction of sulphuric acid chambers (footnote, p. 485).

Alloys of lead, such as solder and pewter (p. 589), are also of considerable importance.

Type-metal, an alloy of lead (about 80 per cent.) and antimony (about 20 per cent.), is readily fusible, expands on cooling (and therefore takes a sharp impression when cast in a mould), and is very much harder than lead. Sometimes a little tin, arsenic, copper, or other metal is added to increase the hardness.

Shot-metal is prepared by melting lead with arsenious anhydride and charcoal. The product, which contains about 0·5 per cent. of arsenic (reduced from its oxide), is poured through a perforated iron basin at the top of a shot-tower, whence it drops into a solution of sodium sulphide. The arsenic makes the lead much harder; the sodium sulphide gives the shot a coating of lead sulphide which protects the metal from oxidation. The spherical shot are separated from the 'tails' by running them down a spiral plane, and are then coated with graphite by shaking them with this material.

Lead is rather rapidly changed when it is exposed to the air, and is converted into a mixture of hydroxide and carbonate,

$$2Pb + 2H_2O + O_2 = 2Pb(OH)_2$$
$$Pb(OH)_2 + CO_2 = PbCO_3 + H_2O;$$

but the carbonate forms a protective layer, and the change is only superficial. Distilled water which contains some dissolved oxygen attacks the metal rapidly, and lead hydroxide (p. 599) passes into solution; but when the distilled water is first freed from dissolved oxygen and carbon dioxide by boiling it for some time, it has no action on the metal.

As all soluble compounds of lead are highly poisonous, and as even the 'insoluble' compounds may be transformed into soluble ones in the human body, the action of various qualities of natural waters on the leaden pipes in which they may be conveyed is of great importance. Soft waters, which contain dissolved oxygen but only small quantities of sulphates and carbonates, and waters from peaty districts which may contain vegetable acids, sometimes become poisonous when passed through lead pipes, owing to their solvent action. Hard waters, however, although they also act on the metal, do not convert it into soluble compounds; the carbonates and sulphates of calcium and magnesium give rise to an insoluble protective coating or scale, which prevents any further appreciable action.

Nitric acid (diluted) acts on lead rather vigorously, forming lead nitrate, oxides of nitrogen being evolved. Hydrochloric acid and sulphuric acid have very little action, even on warming, unless the metal is in a fine state of division.

When lead is heated in the air it gives either lead monoxide or red-lead, according to the conditions under which oxidation occurs.

COMPOUNDS IN WHICH LEAD IS BIVALENT.

Lead monoxide, PbO, is one of the more important lead compounds, and is the basic oxide from which the lead salts are derived. It is prepared on the large scale in the process of cupellation (p. 596) by exposing molten lead to an air-blast; the product melts, and solidifies when cooled to a yellowish-brown crystalline mass known as *litharge*. The same oxide, obtained at lower temperatures, without melting it, and also by heating white lead (p. 600), is yellow, with a tinge of red, and is called *massicot*.

Lead monoxide may be prepared in the laboratory by heating lead nitrate (p. 242),

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2,$$

or lead carbonate, lead hydroxide, red-lead (p. 81), or lead dioxide. It is insoluble in water, and with acids it gives lead salts and water; hence it is used in preparing soluble lead salts such as the acetate (p. 279),

$$PbO + 2C_2H_4O_2 = Pb(C_2H_3O_2)_2 + H_2O.$$

It is also employed in making flint glass (p. 294) and red-lead, and in glazing earthenware.

When lead monoxide is heated with a concentrated solution of sodium hydroxide it gives soluble *sodium plumbite* (see below), but on the saturated solution being cooled, some oxide separates in lustrous yellow crystals.

Lead hydroxide, $Pb(OH)_2$, is obtained as a colourless precipitate when a solution of a lead salt is treated with an alkali hydroxide. It is appreciably soluble in water, giving an alkaline solution, and with acids it yields lead salts; it also gives soluble *plumbites* with sodium or potassium hydroxide,

$$Pb(OH)_2 + NaOH = Pb(ONa)OH + H_2O.$$

The more important soluble lead salts, namely, the *nitrate* (p. 242) and the *acetate* (p. 279), have been described; the insoluble or sparingly soluble salts are prepared from these compounds by precipitation.

Lead chloride, $PbCl_2$, is only sparingly soluble in cold water, but dissolves fairly readily in hot water; it is easily purified by recrystallisation, and forms colourless needles.

Lead bromide, $PbBr_2$, is colourless, but **lead iodide,** PbI_2, is yellow; both salts may be recrystallised from boiling water, in which, however, they are only very moderately soluble.

Lead sulphate, $PbSO_4$, is obtained as a colourless precipitate when sulphuric acid or a solution of a sulphate is added to a solution of a lead salt; it is practically insoluble in water, but dissolves chemically in sodium hydroxide solution. *Lead chromate*, $PbCrO_4$, has already been described (p. 509).

Lead sulphide, PbS, is obtained by precipitation (p. 220); but in presence of much hydrochloric acid a brick-red precipitate, $3PbS,2PbCl_2$, may be first produced.

Lead carbonate, $PbCO_3$, may be obtained by treating a solution of a lead salt with ammonium carbonate; but when sodium carbonate is used the precipitate contains some lead hydroxide, owing to the occurrence of hydrolysis,

$$PbCO_3 + 2H_2O = Pb(OH)_2 + H_2CO_3.$$

Such a precipitate is termed *basic lead carbonate;* it is insoluble in water.

Basic carbonates of lead, having approximately the composition $2PbCO_3$, $Pb(OH)_2$, are prepared on the large scale by various processes, and such preparations are known as *white-lead.*

The oldest process, and the one which gives the best product, is known as the Dutch method. Thin sheet lead, formed into spirals, is placed in earthenware vessels, the spirals resting on ledges some distance above the bottom of the vessel (fig. 111). The vessels contain a little vinegar (acetic acid, p. 279), and are covered by plates of sheet-lead (or by gratings or 'wickets' of lead). These vessels are then packed in manure or spent tan in horizontal layers which are separated by boards, the whole being enclosed in brick chambers. In the course of about three months most of the lead is changed into a dense, porcelain-like mass of white-lead. The chambers are then unloaded, the spirals, sheets, and gratings (which retain their original shape) are crushed in a mill, and any unchanged lead is removed; the white-lead is then ground up and well washed with water, passed into settling-tanks, and finally dried. The manure or spent tan used in this process undergoes 'decay' or fermentation, giving carbon dioxide, and the heat development accompanying this fermentation accelerates the formation of white-lead.

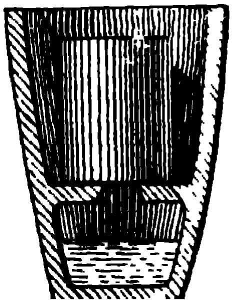


Fig. 111.

Most of the processes for the preparation of white-lead depend on the fact that lead is acted on by acetic acid (vapour) in presence of atmospheric oxygen, giving basic lead acetate, and by water and oxygen, giving lead hydroxide,

$$2Pb + 2C_2H_4O_2 + O_2 = 2Pb(C_2H_3O_2)OH$$
$$2Pb + 2H_2O + O_2 = 2Pb(OH)_2.$$

The basic lead acetate is then decomposed by carbonic acid, giving lead carbonate,

$$Pb(C_2H_3O_2)OH + H_2CO_3 = PbCO_3 + C_2H_4O_2 + H_2O,$$

while the liberated acetic acid acts on fresh quantities of the metal in the manner shown above. These changes may be brought about by suspending sheet lead in a chamber on the floor of which are vessels containing dilute acetic acid, and then passing in steam, air, and carbon dioxide. The product is freed from lead acetate by washing it with water.

The principal use of white-lead is as a paint, for which purpose it is mixed with linseed-oil. This paint has a greater 'covering power' than other white paints (such as zinc oxide, lead sulphate, or barium sulphate), and is extensively used in spite of the danger of lead-poisoning which attends its manufacture, and of the fact that it is liable to become yellow or brownish in town-air, owing to the formation of lead sulphide.

COMPOUNDS IN WHICH LEAD IS QUADRIVALENT.

In lead monoxide, and in the hydroxide and salts derived from it, lead is bivalent; but this metal also gives rise to a few well-known compounds in which it is quadrivalent, and which are of the same type as the corresponding derivatives of carbon, silicon, and tin.

Lead dioxide, PbO_2, is most conveniently prepared in the laboratory by treating red-lead with dilute nitric acid (p. 178), separating the dioxide by filtration, and washing it with water. It may also be obtained by oxidising lead hydroxide suspended in water with sodium hypochlorite or hypobromite (p. 429),

$$Pb(OH)_2 + NaOCl = PbO_2 + NaCl + H_2O.$$

It is a dark-brown powder which gives lead monoxide and oxygen when it is heated (p. 178). When warmed with concentrated hydrochloric acid it gives lead chloride, chlorine, and water,

$$PbO_2 + 4HCl \quad PbCl_2 + Cl_2 + 2H_2O;$$

and with hot concentrated sulphuric acid it gives lead sulphate, oxygen, and water,

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + O_2 + 2H_2O.$$

The salts thus formed are derived from lead monoxide, and not from the dioxide, so that the latter does not act as a basic oxide under the above conditions.

Nevertheless **lead tetrachloride**, $PbCl_4$, and **lead tetracetate**, $Pb(C_2H_3O_2)_4$, salts which are derived from lead dioxide, are known. The tetrachloride is formed when lead dioxide is treated with hydrochloric acid at low temperatures; it is unstable, and its solution evolves chlorine even at ordinary temperatures, lead dichloride being formed. The complex salt (p. 591), $(NH_4)_2PbCl_6$, is more stable.

Towards strong basic oxides, lead dioxide behaves like an anhydride, and gives rise to salts which are derived from orthoplumbic acid, $Pb(OH)_4$, or from metaplumbic acid, $PbO(OH)_2$. Thus, when lead monoxide is heated with excess of sodium carbonate or calcium carbonate in a stream of air an *orthoplumbate* is formed,

$$2PbO + 4Na_2CO_3 + O_2 = 2Na_4PbO_4 + 4CO_2$$
$$2PbO + 4CaCO_3 + O_2 = 2Ca_2PbO_4 + 4CO_2;$$

equimolecular proportions of lead monoxide and sodium carbonate, however, give the *metaplumbate*,

$$2PbO + 2Na_2CO_3 + O_2 = 2Na_2PbO_3 + 2CO_2.$$

Calcium plumbate is decomposed when it is heated at a suitable temperature in a stream of carbon dioxide, the above change being reversed, with liberation of oxygen; this reversible reaction may therefore be utilised for the preparation of oxygen from the air (*Kassner's process*).

Lead dioxide is often called lead *peroxide*; as, however, in some respects it behaves like an anhydride, and resembles manganese dioxide rather than barium peroxide, the name used above seems to be the more suitable one.

Lead dioxide and other oxides of lead are used in accumulators.

Red-lead, Pb_3O_4, is manufactured by carefully heating lead monoxide at about 350° in a free supply of air,

$$6PbO + O_2 = 2Pb_3O_4;$$

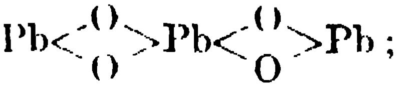
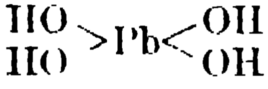
but a product of better colour is obtained by heating white-lead under similar conditions. It has a bright-red colour, and is used as a paint, and in making flint glass, and as a lute.

When heated alone at temperatures above 550°, it gives lead monoxide and oxygen; with dilute nitric acid it gives insoluble lead dioxide and a solution of lead nitrate,

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O;$$

whereas with hot concentrated hydrochloric acid it gives lead chloride and chlorine,

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O.$$

The behaviour of red-lead towards nitric acid seems to show that the substance is really lead orthoplumbate—that is to say, the lead salt of orthoplumbic acid,  $Pb{<}{}^{O}_{O}{>}Pb{<}{}^{O}_{O}{>}Pb$; the action of the nitric acid is to decompose this salt, giving lead nitrate and orthoplumbic acid,  ${}^{HO}_{HO}{>}Pb{<}{}^{OH}_{OH}$, which then passes into its anhydride, lead dioxide, and water.

Red-lead as prepared commercially is not constant in composition, and contains variable quantities of lead monoxide.

The name *lead sesquioxide* and the formula, Pb_2O_3, have been given to a yellowish brown amorphous substance which is obtained by oxidising lead salts with hypochlorites; but the existence of a pure compound of this formula is doubtful. The preparation may be a mixture of PbO and PbO_2, or impure *lead metaplumbate*, $PbPbO_3$.

Lead suboxide, Pb_2O, is a black powder obtained by heating lead oxalate out of contact with the air.

The Relationship between the Members of the Carbon Family.

When the elements of this family are arranged in the order of their atomic weights there is seen to be the same gradual change in physical properties as occurs in the case of other families. This is illustrated by the following data:

	C.	Si.	Ge.	Sn.	Pb.
At. wt. .	12	28·3	72·5	119	207·1
Sp. gr. .	1·6–3·6	2·5	5·5	7·3	11·3
M.p. .	3600° (approx.)	- -	900°	232°	326°

It may be observed, however, that even with respect to the two properties considered, the change is not quite regular; the sp. gr. of silicon (crystalline) is less than that of diamond, and the melting-point of tin is lower than that of lead.

The chemical relationship, as in other families, is closely connected with the fact that the elements have the same valencies; although, with the exception of silicon, they all form oxides of the type XO, in which apparently the elements are bivalent, their characteristic derivatives are the oxides of the type XO_2 and other compounds in which the elements are *quadrivalent.*

The formulæ of some of these typical compounds are given in the following table:

	Hydrides.	Chlorides.	Oxides.	Ortho-acids.	Meta-acids.
C .	CH_4	CCl_4	CO_2	$C(OH)_4$	H_2CO_3
Si .	SiH_4	$SiCl_4$	SiO_2	$Si(OH)_4$	H_2SiO_3
Sn .	—	$SnCl_4$	SnO_2	$Sn(OH)_4$	H_2SnO_3
Pb .	—	$PbCl_4$	PbO_2	$Pb(OH)_4$	H_2PbO_3

The similarity in type of their more important compounds, in consequence of which corresponding compounds are closely related, is accompanied by a gradual change in the chemical properties of any series of such corresponding derivatives; and this change is of the same kind as that noted in the case of the nitrogen family; that is to say, the non-metallic character of the element wanes, the metallic character waxes, as the atomic weight increases.

Thus only carbon and silicon form volatile hydrides, CH_4 and SiH_4 respectively, and of these the latter is the less stable. Carbon and silicon do not form *basic* oxides of the type XO; germanous oxide, GeO, is only feebly basic; but SnO and PbO both give rise to stable salts, of which those of lead are less readily hydrolysed than those of tin. The chlorides, XCl_4, are not salts, but acid chlorides; this is clearly so in the case of CCl_4 and $SiCl_4$, both of which undergo a non-reversible hydrolysis;* whereas, owing to the increase in the metallic character of the elements, $SnCl_4$ and $PbCl_4$, although hydrolysed by water, have in some respects the properties of salts.

The oxides XO_2 are all anhydrides; although only carbon dioxide unites directly with water, and most of the acids derived from these oxides are not known in a pure state, salts corresponding with both the ortho- and the meta-acids of most of the elements are known. From the behaviour of these salts it may be inferred that the strength of the acid gradually diminishes in passing from carbon to lead.

THE TITANIUM SUB-FAMILY.

The elements of this sub-family, together with those of the carbon sub-family, form Family IV. of the periodic system (p. 720).

Titanium, Ti, at. wt. 48·1, occurs as the dioxide TiO_2 in many iron ores, and is often contained in pig-iron; the dioxide is also found as the mineral *rutile*. The metal may be obtained by reducing the oxide with carbon in the electric furnace. One of its most striking properties is that it combines readily with nitrogen at 800°, forming a **nitride** (Ti_2N_2?).

Zirconium (Zr), **Cerium** (Ce),† and **Thorium** (Th) also belong to the titanium sub-family, and occur together in *monazite sand*, which is a particularly complex mixture of minerals found in various parts of the world (Carolina, Brazil, the Ural Mountains, Australia). This mineral contains *cerium phosphate* and *thorium*

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* Carbon tetrachloride, CCl_4, is not appreciably acted on by cold water, but it is completely hydrolysed when it is heated with water at about 250° in sealed tubes.

† Cerium may possibly belong to the nitrogen family.

silicate, $ThSiO_4$, and from it the nitrates of cerium and thorium are prepared on the large scale.

The Welsbach incandescent mantles are prepared by dipping a fabric of pure cotton into a solution of thorium nitrate which also contains about 1 per cent. of cerium nitrate; the mantles are then ignited, whereby the nitrates are converted into the oxides *thoria*, ThO_2, and *ceria*, CeO_2, respectively.

The *mixture* of oxides thus obtained gives out a very bright light when it is heated in a Bunsen-flame, whereas either of the oxides alone, or a mixture containing a larger or smaller proportion than 1-2 per cent. of ceria, is far less efficient. Although it is known that the light emission is almost entirely due to the ceria, the action of the latter is not fully understood. It has been suggested that the ceria acts as a catalyst, and that its particles are raised to a very high temperature because the heat of the reaction is concentrated on them, while they are prevented to a great extent from losing this heat by the non-conducting particles of thoria.

A mixture of the oxides of zirconium, cerium, and several other 'rare earths,' made into the form of a rod, is used in the *Nernst lamp*; at ordinary temperatures the rod is a non-conductor of electricity, but when it is heated (by an automatic electric heater) its conductivity is increased sufficiently to allow of the passage of a current. The rod is thus finally raised to incandescence.

CHAPTER LVI.

The Boron Family.

This family includes a number of elements, but of these only boron and aluminium are commonly met with; and even boron is practically unknown except in the form of a few important compounds, such as borax and boric acid.

BORON, B; AT. WT. 11.

The element boron occurs in nature only in a combined state and in relatively very small quantities; but in the form of boric acid, or of salts derived from this acid, it is very widely diffused, and is found in nearly all plants.

Free boric acid is volatile in steam, and in parts of Tuscany, in the Lipari Islands, and in other volcanic regions, it is present in small quantities in the steam or water-vapour which escapes from fissures in the earth. Salts of boric acid (or of complex acids derived from it) are found in various parts of the world. *Borax*, tincal or sodium tetraborate, for example, occurs in an immense bed, and in the borax-lake in California; also in lakes in Thibet, India, China, and other countries. *Boracite* (a magnesium salt) and *borocalcite* or calcium tetraborate, $CaB_4O_7, 6H_2O$, also serve as sources of boron compounds.

Borax, $Na_2B_4O_7, 10H_2O$, the most important of these compounds, is the sodium salt of **tetraboric acid,** a substance which is derived from orthoboric acid,

$$4B(OH)_3 = H_2B_4O_7 + 5H_2O.$$

It is obtained on the large scale by recrystallising native Californian borax from hot water; also by treating boric acid (see below) with sodium carbonate. It is readily soluble in water, and its solution has an alkaline reaction to litmus, owing to the occurrence of hydrolysis,

$$Na_2B_4O_7 + H_2O = NaOH + NaHB_4O_7.$$

When borax is heated it first swells up and becomes anhydrous, and then melts to a colourless liquid, which readily dissolves metallic oxides, forming borates. Hence borax is used as a flux in soldering, and in glazing fine earthenware; it is also used in the laboratory in the form of a 'borax bead' in testing for metals, as some metallic oxides give borates of a characteristic colour. Borax is employed in laundry-work to give stiffness and a glaze to linen, &c.

Boric acid, or orthoboric acid, $B(OH)_3$, is obtained on the large scale from the steam which escapes from the ground in Tuscany and elsewhere. The water of the small pools formed by the condensation of the steam is evaporated, the heat of the natural steam jets being utilised as far as possible; the concentrated solution of boric acid is then left to crystallise.

Boric acid is also prepared by treating boracite and other such minerals with hydrochloric acid, and then recrystallising the product. It is obtained in the laboratory in a similar manner by adding hydrochloric acid to a hot concentrated solution of borax, and then cooling the mixture,

$$Na_2B_4O_7 + 2HCl = 2NaCl + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O = 4B(OH)_3.$$

Boric acid crystallises in colourless scales, which easily slide over one another, and therefore feel slippery or soapy. It is readily soluble in water, but its aqueous solution has only feeble acid properties; so much so that it hardly changes the colour of blue litmus.

Boric acid is used as an antiseptic in pharmacy and also in the preservation of food.

Boric acid imparts a green colour to a non-luminous flame. When a borate is mixed with a little concentrated sulphuric acid and some alcohol in a basin, and the alcohol is then lighted, its flame is tinged with green, owing to the volatilisation of the *free* boric acid which has been liberated by the sulphuric acid. This flame-test is used for the detection of borates.

When boric acid is heated (at 100°) it first gives **metaboric acid**, $BO{\cdot}OH$, then (at 140°) **pyroboric** or **tetraboric acid**, $B_4O_5(OH)_2$,* and finally (at a red heat) boric anhydride, B_2O_3.

Boric anhydride, B_2O_3 (boron trioxide), is a vitreous solid; being volatile only at a white heat, it liberates other anhydrides from their salts at high temperatures, just as does silica or silicic anhydride (p. 360),

$$Na_2SO_4 + 2B_2O_3 = Na_2B_4O_7 + SO_3.$$

It combines with water with some vigour, giving boric acid.

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* The molecular formula of metaboric acid is probably $(HBO_2)_2$, and its structural formula, $HO-B\langle{}^{O}_{O}\rangle B-OH$. Pyroboric acid may be represented by the structural formula, $HO-B\langle{}^{O}_{O}\rangle B-O-B\langle{}^{O}_{O}\rangle B-OH$. Boric anhydride is probably a polymeride of the oxide, B_2O_3 (compare silica, p. 583).

Boron may be obtained by heating the oxide with magnesium,

$$B_2O_3 + 3Mg = 2B + 3MgO;$$

but the separation of the boron from the large proportion of *magnesium boride* which is also produced is a very difficult task. After careful purification (which involves treatment with hydrofluoric acid) the product is obtained as a light-brown *amorphous* powder of sp. gr. 2·45. *Crystallised* boron is obtained by dissolving the amorphous element in molten aluminium; when the aluminium is afterwards treated with hydrochloric acid crystals of boron remain, but their purity is doubtful.

Boron burns to the trioxide when it is heated in oxygen, and it also combines with chlorine, nitrogen, and many other elements at high temperatures.

Boron hydride, BH_3, is not known in a pure state; when magnesium boride is treated with hydrochloric acid a mixture of several hydrides of boron is formed.

Boron trichloride, BCl_3, may be prepared by heating boron in a stream of dry chlorine; it is a colourless, mobile liquid (b.p. 18°), and is completely hydrolysed by water.

Boron nitride, BN, is obtained as an almost colourless powder when boron is heated at about 1300° in nitrogen or in ammonia. It is not decomposed when it is heated alone or in the air, even at high temperatures, but it is decomposed by boiling water, giving ammonia and boric acid,

$$BN + 3H_2O = NH_3 + B(OH)_3.$$

ALUMINIUM, Al; AT. WT. 27·1.

This very abundant element occurs, with rare exceptions, in combination with oxygen. The oxide is found in small quantities in a free state in various forms (ruby, sapphire, corundum, p. 294); but as a rule it is combined with silica, forming aluminium silicate, one of the most important components of the earth's crust. During the disintegration of the felspars, such as orthoclase, $K_2O, Al_2O_3, 6SiO_2$, and albite,

Na_2O, Al_2O_3, $6SiO_2$ (pp. 291, 584), the micas,* and other silicates, the alkali silicates are dissolved, and beds of almost pure aluminium silicate, $Al_2Si_2O_7$, $2H_2O$ (kaolin or china-clay), may be formed, as already mentioned (p. 291).

Some other native aluminium compounds are referred to later; the only important one which does not contain combined oxygen is cryolite (p. 402).

At one time aluminium was prepared commercially by heating sodium aluminium chloride (a complex salt corresponding with the fluoride, cryolite) with sodium,

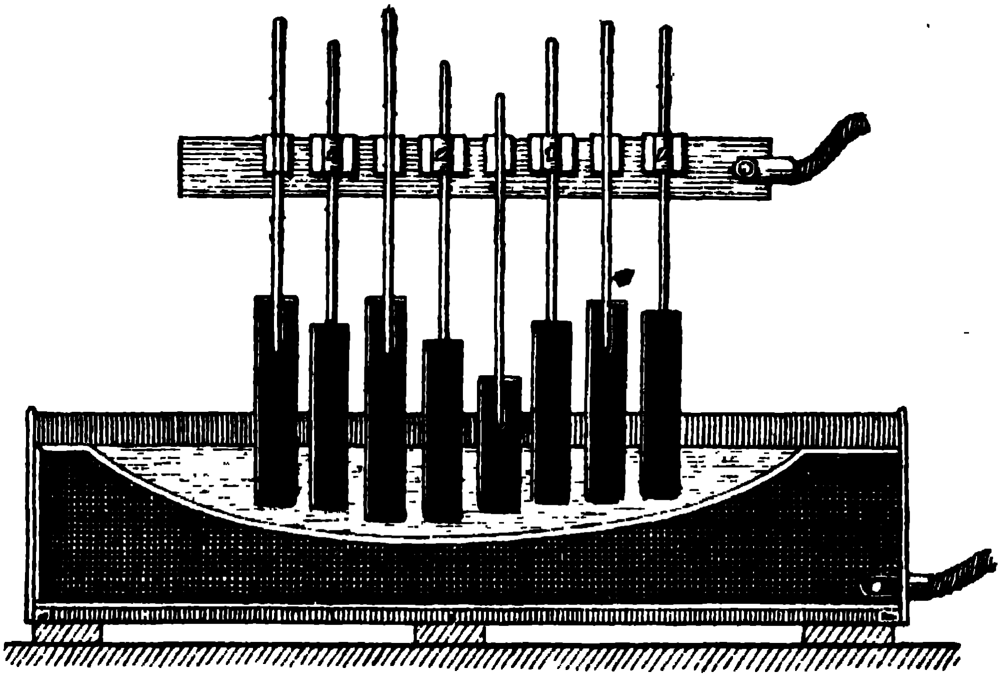

Fig. 112.

$$3NaCl, AlCl_3 + 3Na = Al + 6NaCl,$$

but it is now manufactured by the electrolysis of aluminium oxide.

Rectangular iron vessels (6 × 8 ft., fig. 112), heavily lined with graphite, are partly filled with cryolite. The positive electrode consists of a number of cylindrical graphite rods which dip into the cryolite, while the iron vessel and its graphite lining form the negative electrode. The current is supplied by dynamos worked by water-power. When the current is passed the resistance of the cryolite causes a development of heat which soon melts the mineral. At this stage aluminium oxide, usually prepared from bauxite (p. 614), is introduced into the fused mass. Electrolysis then occurs with liberation of aluminium at the cathode and oxygen at the anode. The molten aluminium collects at the bottom of the vessel, and is run off from time to time through the tap-hole, which is closed meanwhile with a graphite plug. The liberated oxygen escapes as gas or combines with the carbon of the anodes. Fresh quantities of alumina are added at intervals, so that the process is continuous.

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* Mica sometimes occurs in very large crystals which can be split into transparent sheets.

Aluminium bronze, an important alloy of aluminium and copper, is manufactured in a similar manner, some copper being added with the alumina. The properties of the product depend on the relative proportions of the two metals; an alloy containing only 5 per cent. of aluminium has the colour of gold. Those containing about 12 per cent. of aluminium give homogeneous castings, and are very tough and elastic; they take an excellent polish and do not tarnish on exposure to the air.

Aluminium has a bright, slightly bluish, silvery lustre, and its sp. gr. is 2·6. It is hard, tough, and malleable, and melts at about 654°. It does not alter appreciably on exposure to a moist atmosphere, and the very finely divided metal, mixed with oil, is extensively used as a paint for iron and steel work. The metal is also used for making many small articles (pans, cameras, trays, brush-frames, cups) and for the manufacture of any apparatus which must be both light and strong. Its use in the preparation of manganese and chromium has already been mentioned (pp. 443, 502; compare also thermite, p. 704); sometimes for these purposes an alloy of aluminium and calcium is used, as the development of heat is then greater than when aluminium alone is employed, and the 'slag' of calcium aluminate is more readily fusible than alumina.

Aluminium in a compact form may be melted in oxygen without undergoing more than a superficial oxidation, as it is protected by the layer of oxide, but thin foil burns brilliantly. The finely divided metal is also oxidised by boiling water, hydrogen being evolved; it is rapidly attacked by a hot solution of sodium hydroxide, with formation of hydrogen and a solution of sodium aluminate,

$$2Al + 6NaOH = 3H_2 + 2Al(ONa)_3.$$

It is not acted on appreciably by nitric acid, and dilute sulphuric acid attacks it only very slowly; but with hot concentrated acid it gives aluminium sulphate, sulphur dioxide, and water.

It is readily acted on by hydrochloric acid, with formation of aluminium chloride and hydrogen,

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

*Aluminium Amalgam.**—When a little mercury is placed on a bright sheet of aluminium and well rubbed on the sheet with a damp rag, the aluminium becomes coated with a thin film of mercury. By breathing on the sheet, and thus forming a film of moisture, a chemical action is set up; the aluminium dissolved in the mercury decomposes the water, giving aluminium hydroxide, which rises as a bulky white powder from the surface of the metal.

Aluminium may also be coated with mercury by placing it for a few moments in a dilute solution of mercuric chloride (p. 632); the product (*aluminium amalgam*) is used as a reducing agent, since it rapidly decomposes water, with formation of hydrogen and aluminium hydroxide.

Aluminium chloride, $AlCl_3$, is prepared in the laboratory by passing dry chlorine or hydrogen chloride over heated aluminium foil contained in a long glass tube.

It is prepared on the large scale by passing chlorine over a *mixture* of carbon and aluminium oxide (compare p. 580), but a high temperature is required,

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

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* The term 'amalgam' is applied to alloys of mercury.

In both cases the product volatilises and is condensed in a receiver from which moisture is excluded.

Aluminium chloride is a colourless crystalline substance, but the commercial article is generally yellow. It sublimes readily (below 185°), and its vapour density at about 800° corresponds with the formula $AlCl_3$.* It is often used in preparing carbon compounds.

When aluminium chloride is placed in water a great development of heat occurs and the salt is hydrolysed; when the solution is evaporated hydrogen chloride escapes and some hydroxide is formed,

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl.$$

Most of the other important compounds of aluminium are prepared from clay (p. 291), from which aluminium sulphate or an alum is first manufactured in the manner described below; cryolite (p. 402) and bauxite (p. 614) are also used as sources of aluminium compounds.

Aluminium hydroxide, $Al(OH)_3$, is formed as a colourless gelatinous precipitate when an aluminium salt, such as the sulphate, is treated with ammonium hydroxide or sodium hydroxide in aqueous solution,

$$Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3 + 3Na_2SO_4.$$

It is likewise formed when the carbonates are used instead of the hydroxides, because aluminium carbonate, if produced, is completely hydrolysed by water,

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2.$$

The freshly precipitated hydroxide dissolves chemically in acids, forming soluble aluminium salts, and also in sodium hydroxide solution, giving soluble *sodium aluminate*,

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O;$$

but when it is dried it begins to lose the elements of water, and becomes less readily soluble. A 'colloidal solution' of aluminium hydroxide may be obtained by dissolving the freshly precipitated hydroxide in an aqueous solution of aluminium chloride, and then submitting the solution to dialysis (p. 326).

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* At lower temperatures the results show that the vapour is a mixture of molecules of $AlCl_3$ and Al_2Cl_6.

Although towards strong acids (but not towards weak acids such as carbonic acid) aluminium hydroxide behaves as a basic hydroxide, it acts as an acid towards strongly basic hydroxides (but not towards ammonium hydroxide), and forms *aluminates* which are derived from $Al(OH)_3$, and *meta-aluminates* which are derived from $AlO{\cdot}OH$. The alkali aluminates (or the meta-aluminates) are formed when the hydroxide is treated with excess of an alkali hydroxide (p. 613), or when the oxide is fused with excess of sodium carbonate,

$$Al_2O_3 + 3Na_2CO_3 = 2Al(ONa)_3 + 3CO_2.$$

The normal alkali aluminates are hydrolysed by water,

$$Al(ONa)_3 + 2H_2O = Al(OH)_2{\cdot}ONa + 2NaOH,$$

and the substances thus produced then decompose, giving the soluble meta-aluminates; even these compounds undergo hydrolysis, and they are completely decomposed by carbonic acid, aluminium hydroxide being precipitated,

$$2AlO{\cdot}ONa + H_2CO_3 + 2H_2O = 2Al(OH)_3 + Na_2CO_3.$$

Aluminium hydroxide occurs in nature as *hydrargyllite*, and meta-aluminic acid as *diaspore*, $AlO{\cdot}OH$. *Bauxite* is an earth which has the composition $Al(OH)_3$, $AlO{\cdot}OH$, but it often contains ferric oxide, and has then a brick-red colour.* It is found in large quantities in various parts of the world, and is used for the manufacture of aluminium and other products.

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* Pure aluminium hydroxide is prepared from such samples of bauxite by fusing the mineral with sodium carbonate, extracting the soluble sodium aluminate with water (whereby ferric oxide is left behind), and then precipitating the aluminium hydroxide by passing carbon dioxide into the solution (see above).

Several meta-aluminates are found in nature, as, for example, magnesium meta-aluminate or *spinelle*, $(AlO{\cdot}O)_2Mg$, and zinc meta-aluminate or *gahnite*, $(AlO{\cdot}O)_2Zn$; they all crystallise in the same form and are classed as the *spinelles*.

Aluminium oxide (alumina), Al_2O_3, is obtained by igniting the precipitated and well-washed hydroxide, prepared by the methods given above. It is a colourless amorphous substance which is moderately easily attacked by acids and by sodium hydroxide solution, giving aluminium salts or an aluminate as the case may be. When, however, it is very strongly heated it becomes denser (and possibly crystalline), and is then only very slowly attacked by acids. Crystalline alumina (ruby, sapphire, corundum, &c.) is insoluble in acids, but is converted into soluble aluminates when it is fused with sodium hydroxide. Aluminium oxide is not reduced by carbon except at the high temperature of the electric furnace.

Aluminium oxide, prepared by melting dehydrated bauxite in an electric furnace, is sold under the name of *alundum* for use as an abrasive. It is harder than the native forms of alumina, and is used for cutting or drilling rubies, sapphires, &c., and in making grinding-wheels (compare carborundum, p. 581).

Aluminium sulphate, $Al_2(SO_4)_3, 18H_2O$, is manufactured by dissolving bauxite in sulphuric acid.

It is also produced from clays and shales and other materials in large quantities. The clay or shale (p. 292) is first extracted with dilute hydrochloric acid in order to remove some of the iron compounds; it is then dried and roasted in order to disintegrate it, to get rid of vegetable matter (coal, bitumen), and to oxidise iron pyrites. The material is afterwards ground up and heated in leaden pans with moderately concentrated sulphuric acid; the solution is separated from the silica and other insoluble matter, and the aluminium sulphate crystallised out.

Cryolite (a complex salt, p. 591) is heated with limestone,

$$AlF_3,3NaF + 3CaCO_3 = Al(ONa)_3 + 3CaF_2 + 3CO_2,$$

and the product is treated with water; the solution of the sodium aluminate is separated from the insoluble calcium fluoride, and carbon dioxide is passed through it in order to precipitate aluminium hydroxide (see p. 614). The latter is then separated by filtration or decantation and dissolved in sulphuric acid, while the sodium carbonate solution is evaporated.

Aluminium sulphate is readily soluble in water, but the solution is strongly acid to litmus, as the salt undergoes hydrolysis, giving free acid and soluble basic salts,

$$Al_2(SO_4)_3 + 2H_2O = Al_2(SO_4)_2(OH)_2 + H_2SO_4.$$

It has already been stated (pp. 294, 295) that an important series of *double salts* called the *alums* may be obtained by adding certain sulphates to solutions of aluminium sulphate, and then crystallising the products from the concentrated solutions. The alums have the formula $Al_2(SO_4)_3$, X_2SO_4, $24H_2O$, where X represents Na, K, (NH_4), or certain other *uni*valent metals or basic radicles. It is possible also to prepare double salts of this particular type from the sulphates X_2SO_4 by mixing them in aqueous solution with sulphates of tervalent metals other than aluminium. Thus a double salt, $Cr_2(SO_4)_3$, K_2SO_4, $24H_2O$, may be prepared from the sulphates of chromium and potassium. This product has the same crystalline form as ordinary potash alum, and is therefore classed as an alum, although it does not contain an aluminium salt. The term *alum*, therefore, is used in a wide sense, and is applied to double salts of the type $M_2(SO_4)_3$, X_2SO_4, $24H_2O$, where M is a metal such as Al, Cr, Fe, Mn, in the tervalent state, and X a metal or basic radicle in the univalent state; when the alum does not contain aluminium sulphate it is named according to the two sulphates of which it is composed. Thus the double salt $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$ is called ferric ammonium alum.

The alums are all isomorphous (p. 324). They are extensively used as mordants in the dyeing industries, and are also employed in paper-making.

Alum stone, or alunite, is a crystalline substance of the composition K_2SO_4, $Al_2(SO_4)_3$, $4Al(OH)_3$, produced naturally by the action of sulphur dioxide (of volcanic origin) on felspar and similar rock components. It is insoluble in water; but when it has been heated it is then acted on by water, giving a solution of potash alum and a residue of alumina.

Although aluminium is distinctly metallic in its physical properties, it does not show a very marked metallic character in its chemical behaviour. Its chloride is easily hydrolysed; its hydroxide does not give salts with very weak acids, and behaves like an acid towards strong bases.

Aluminium sulphide, Al_2S_3, prepared by heating aluminium with sulphur, is readily hydrolysed, giving aluminium hydroxide and hydrogen sulphide.

Ultramarine, or *lapis lazuli*, is a silicate of aluminium and sodium, which also contains combined sulphur; it occurs as a blue, green, or violet crystalline mineral, which at one time was highly prized.

Artificial ultramarine of a beautiful blue colour, and preparations of other colours, are now manufactured by carefully heating a very intimate mixture of kaolin, sodium carbonate, charcoal, and sulphur in absence of air. The green product is washed with water, dried, mixed with sulphur, and gently roasted in the air until it acquires the desired blue colour. The nature of ultramarine is not exactly known. The material is used as a paint, and in laundry-work; it is easily attacked by acids, and then loses its colour.

OTHER ELEMENTS OF THE BORON FAMILY.

Gallium, Ga, at. wt. 69·9, and **indium,** In, at. wt. 114·8, are both rare metals which occur in small quantities in a combined form in some varieties of zinc-blende. Both elements resemble aluminium in chemical properties, the usual gradation being shown; but in addition to forming compounds in which they are tervalent—as, for example, the chlorides $GaCl_3$, $InCl_3$, and the oxides Ga_2O_3, In_2O_3—gallium forms a chloride, $GaCl_2$, while indium forms not only an oxide, InO, and a chloride, $InCl_2$, but also a chloride, InCl. The existence of gallium was predicted by Mendeléeff (p 726.).

Thallium, Tl, at. wt. 204, also occurs in zinc-blende; and while resembling aluminium and the other members of the sub family in forming compounds such as $TlCl_3$ and Tl_2O_3, in which the metal is tervalent, it also gives rise to a series of thallous compounds, such as Tl_2O, $TlOH$, and $TlCl$. In the thallous-compounds the metal is univalent, and these compounds show a close relationship to the corresponding derivatives of the (univalent) alkali metals. **Thallous hydroxide,** for example, is readily soluble in water and is a strong base; **thallous chloride,** on the other hand, is only very sparingly soluble in water, and resembles silver chloride rather than sodium chloride.

In the boron sub-family, as in several others, the gradual change in the properties of the elements with increasing atomic weight may be summarised in the statement that the elements gradually become more and more distinctly metallic in character.

The typical compounds of this sub family are those in which the elements are tervalent.

Scandium (Sc), **yttrium** (Y), and **lanthanum** (La) form a sub-family, which together with the boron sub-family constitute Family III. of the periodic system: they occur in monazite sand (p. 605). The existence of scandium was predicted by **Mendeléeff.**

CHAPTER LVII.

The Magnesium Family.

Four well-known metals, namely, magnesium, zinc, cadmium, and mercury, are classed together in this family, which also includes the element beryllium (or glucinum). All these elements occur in nature exclusively in a combined form, with the exception of mercury, a small quantity of which is also found in the free state.

Beryllium, Be, at. wt. 9·1, occurs as metasilicate mixed with aluminium metasilicate in the mineral *beryl*, $3BeSiO_3, Al_2(SiO_3)_3$, which when coloured green, probably by traces of chromium silicate, forms the gem known as the emerald. Beryllium is a metal (sp. gr. 1·9) resembling magnesium in properties, but it differs from the latter in a few respects; thus its *hydroxide*, $Be(OH)_2$, although basic, has feeble acid properties and dissolves chemically in sodium hydroxide solution, and its *carbonate*, $BeCO_3$, is soluble in water.

MAGNESIUM, Mg; AT. WT. 24·3.

Magnesium is an element which in many respects resembles calcium, and it occurs in nature in large quantities in the form of its *carbonate*, $MgCO_3$ (p. 272); it also occurs as magnesium silicate in many rock materials (asbestos, talc, meerschaum). In addition, it is found in the form of certain soluble salts, such as the sulphate (p. 226) and the chloride, in deposits formed by the evaporation of lakes, and in many natural waters.

The largest deposits of such compounds are those found near Stassfurth, which contain *carnallite*, $MgCl_2, KCl, 6H_2O$; *kieserite*, $MgSO_4, H_2O$; and *kainite*, $K_2SO_4, MgSO_4, MgCl_2, 6H_2O$ (p. 676).

Magnesium cannot be obtained by reducing its oxide with charcoal; it is manufactured by the electrolysis of a fused mixture of magnesium and potassium chlorides.

This mixture, prepared by dehydrating carnallite, is melted in an iron crucible, which itself forms the negative electrode; a rod of graphite dipping into the fused mass forms the positive electrode. Chlorine is liberated at the positive and magnesium at the negative electrode; potassium is not set free so long as any magnesium chloride is present, because potassium liberates magnesium from magnesium chloride.

Magnesium is very like silver in appearance, but its sp. gr. is only 1·75. It is malleable and hard. It melts at about 800° and distils at a white heat. It is not used for the preparation of any important alloys, or for the manufacture of any metallic articles; but it is employed in making fireworks and flashlights, and it is often used in the laboratory.

Magnesium tarnishes on exposure to the air, but the film of oxide or basic carbonate which is formed protects the metal from further action; it is only very slowly acted on by boiling water, giving hydrogen and magnesium hydroxide,

$$Mg + 2H_2O = H_2 + Mg(OH)_2.$$

It is very readily attacked by all common acids, giving hydrogen and a magnesium salt. It burns in the air and even in gases which contain combined oxygen, forming magnesium oxide; thus, if a piece of burning magnesium ribbon is lowered into a flask in which water is boiling vigorously, the metal continues to burn in the *steam*, and the liberated hydrogen burns at the mouth of the flask,

$$H_2O + Mg = MgO + H_2.$$

A piece of burning magnesium ribbon lowered into a vessel containing carbon dioxide also continues to burn, but rather fitfully, and the liberated carbon is deposited on the magnesium oxide which is formed,

$$CO_2 + 2Mg = 2MgO + C.$$

Magnesium, like aluminium, is a very powerful reducing agent, as shown by the examples just given and also by its action on silica (p. 577) and boron trioxide (p. 609).

In conjunction with an acid it may be used as a reducing agent at ordinary temperatures; ferric chloride, for example, is reduced to ferrous chloride when its solution in dilute hydrochloric acid is treated with magnesium.

Magnesium combines vigorously with the halogens and with many other elements; magnesium silicide (p. 577) and magnesium nitride (p. 517) have already been mentioned. The *sulphide*, MgS, prepared by heating the metal with sulphur, is decomposed by boiling water, giving magnesium hydroxide and hydrogen sulphide.

The light given out during the burning of magnesium is very rich in actinic (chemically active) rays; hence its use in photography.

Magnesium oxide (magnesia), MgO, may be prepared by heating the hydroxide, carbonate, or nitrate; the substance obtained by heating the metal in the air always contains some magnesium nitride. The oxide is a white solid, and is used as a lining for crucibles and furnaces, as it does not melt even at the high temperatures reached in an electric furnace. It is insoluble in water, but it slowly combines with water to form magnesium hydroxide, which is appreciably soluble; acids act on it rapidly, forming the corresponding magnesium salts.

Magnesium hydroxide, $Mg(OH)_2$, is obtained as a colourless gelatinous precipitate when a solution of a magnesium salt is treated with a solution of sodium hydroxide,

$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl.$$

Ammonium hydroxide also precipitates magnesium hydroxide from solutions of magnesium salts,

$$MgSO_4 + 2NH_4{\cdot}OH \longleftrightarrow Mg(OH)_2 + (NH_4)_2SO_4\,;$$

but precipitation is incomplete, and in presence of a large proportion of an ammonium salt no precipitate whatever is produced.

This is due partly to the fact that the reactions are readily reversible, partly to the formation of stable soluble compounds by the combination of the magnesium and ammonium salts. (Compare p. 591.)

Magnesium hydroxide is only very sparingly soluble in water; its solution has an alkaline reaction to litmus, and absorbs carbon dioxide with formation of a basic magnesium carbonate.

The salts of magnesium correspond with the oxide, MgO. The soluble ones, of which the chloride and sulphate are important, may be prepared by treating the metal, the oxide, or the carbonate (native magnesite) with the required acid; the insoluble salts, of which the carbonate and magnesium ammonium phosphate may be mentioned, may be prepared by precipitation. The soluble salts have a bitter taste. The sulphate and a basic carbonate (p. 623) are used in medicine.

Magnesium chloride, $MgCl_2$, is deliquescent, and very readily soluble in water. When its aqueous solution is boiled, hydrochloric acid escapes and a basic salt remains,*

$$MgCl_2 + H_2O = MgCl{\cdot}OH + HCl.$$

As pure anhydrous magnesium chloride cannot be prepared by evaporating aqueous solutions of the salt, the solutions are mixed with ammonium chloride and evaporated; magnesium ammonium chloride, $MgCl_2, 2NH_4Cl, 6H_2O$, is then deposited in crystals. When this double salt is ignited, it gives a residue of anhydrous magnesium chloride as, first the water of hydration escapes, and afterwards the ammonium chloride volatilises.

Magnesium chloride is decomposed to some extent when it is heated in a stream of moist air, and chlorine is evolved together with hydrogen chloride,

$$4MgCl_2 + 2H_2O + O_2 = 4MgO + 4HCl + 2Cl_2.$$

Magnesium sulphate, $MgSO_4, 7H_2O$ (Epsom salt, pp. 226, 281), forms double salts with the sulphates of potassium and ammonium; these are of the type $MgSO_4, X_2SO_4, 6H_2O$, where X represents K or (NH_4), and are readily soluble in water (p. 491).

Magnesium nitrate, $Mg(NO_3)_2$, is readily soluble in water; when ignited it gives the oxide.

Magnesium carbonate, $MgCO_3$, which occurs as magnesite, and, mixed with calcium carbonate, as dolomite (p. 272), cannot be obtained in a pure state by treating a solution of a magnesium salt with sodium carbonate, as the product is hydrolysed to some extent, and a mixture of carbonate and hydroxide (a basic carbonate, *magnesia alba*) of variable composition is produced.

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* Owing to the occurrence of this hydrolysis, sea-water (which always contains magnesium chloride) is not suitable for use in steam-boilers, as the liberated acid attacks the iron.

This precipitate may be converted into the normal carbonate by suspending it in water and passing carbon dioxide into the liquid; with excess of carbon dioxide it is converted into soluble *magnesium hydrogen carbonate*, $Mg(HCO_3)_2$ (p. 273).

Magnesium ammonium phosphate, $Mg(NH_4)PO_4$, has already been mentioned (p. 550).

ZINC, Zn; AT. WT. 65·4.

Zinc does not occur in nature in the form of salts which are soluble in water, and the principal sources of the metal are *zinc-blende*, ZnS (p. 221), and *calamine*, $ZnCO_3$, a yellow, stony material; but *zincite* or *red zinc ore*, ZnO (coloured by oxides of manganese and iron), is also used.

The principles on which the extraction of zinc is based are as follows: Zinc sulphide is converted into zinc oxide and sulphur dioxide when it is heated in the air (roasted),

$$2ZnS + 3O_2 = 2ZnO + 2SO_2;$$

and zinc carbonate is converted into the oxide when it is gently heated,

$$ZnCO_3 = ZnO + CO_2.$$

Zinc oxide is reduced when it is very strongly heated with coal,

$$ZnO + C = Zn + CO,$$

and at the very high temperature necessary for this reduction the metal distils, leaving behind the earthy matter and other materials.

An intimate mixture of zinc oxide (roasted ore) and coal is introduced into fire-clay cylinders or retorts such as those shown in fig. 113. These vessels, the larger of which takes 1½–2 cwts. of ore, are arranged in a furnace in such a manner that the movable adapters or receivers (*a*, *a*) project through the walls. On heat being applied, carbon monoxide is evolved, and if the zinc ores contain cadmium oxide, as is often the case, this oxide is reduced and the metal volatilises before the zinc begins to come over to any great extent. As soon as all the cadmium has distilled the receiver is changed. The product which then condenses consists partly of liquid zinc, partly of zinc-powder (*zinc-dust*), and one of the principal difficulties met with in the extraction of the metal is to prevent its condensation in a powdery form.

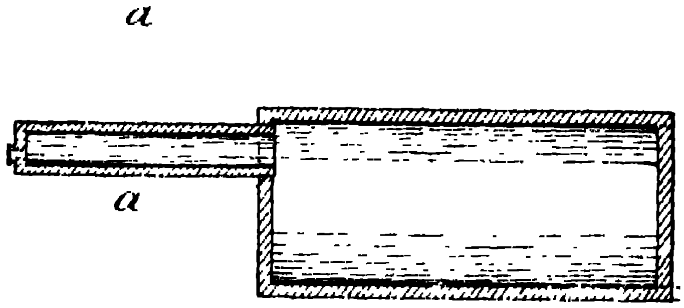

Fig. 113.

The crude zinc is purified mechanically by keeping it melted for some time. The lighter impurities rise to the surface and are skimmed off, while the heavier ones (lead and iron) sink to the bottom. The metal is then ladled out, leaving the lower portions (a mixture of lead, zinc, and iron); but it may still contain as much as 1·5 per cent. of lead, some iron, and traces of arsenic. The lead and iron may be eliminated by distilling the zinc; in order to get rid of arsenic, the melted metal may be stirred with magnesium chloride, when the arsenic volatilises as arsenic trichloride.

As native zinc compounds dissolve chemically in acids, many attempts have been made to obtain zinc by treating the ores with acids and then submitting the salts to electrolysis; so far, these processes do not seem to be very successful.

Zinc has a bluish-grey metallic lustre and a sp. gr. of about 7·1. It is crystalline, melts at about 420°, and boils at about 950°; it is not very malleable at ordinary temperatures, and is, in fact, brittle when it contains certain impurities; but even the impure metal is malleable at 100–140°, and may then be rolled into sheets; it becomes brittle again at about 205°.

It is employed in making small castings; in the form of sheets, it is used for the manufacture of gutters, cisterns, pipes, &c., and for roofing purposes. It is also employed for 'galvanising' iron, in making various alloys such as brass, in electric batteries, and in Parke's process for desilverising lead.

Galvanised iron is manufactured by immersing carefully cleaned sheets of wrought-iron in melted zinc, the surface of which is covered with ammonium chloride, as this substance dissolves oxide of zinc.

The coating of zinc on galvanised iron prevents the rusting of the iron even when the coating gets scratched and the iron itself is exposed to atmospheric influences. This is not so in the case of tin-plate, for if the coating of tin gets damaged, so that iron is exposed, rusting proceeds very rapidly, causing the tin to peel off. The difference between the two cases is due to the fact that in the electric couple or galvanic battery (p. 297), formed from the iron and the other metal in conjunction with impure water, the iron is the positive electrode when in contact with zinc, but the negative electrode when in contact with tin; in the former case, therefore, the zinc, in the latter the iron, passes into solution.

Zinc is only slowly attacked by moist air, and it then becomes coated with a layer of basic carbonate, which protects the metal from further change; when strongly heated in the air it burns with a very bright bluish flame, giving clouds of zinc oxide. Pure zinc is very slowly attacked by hydrochloric or sulphuric acid at ordinary temperatures, but it is vigorously acted on by nitric acid, giving zinc nitrate. When in contact with certain other metals, such as copper or platinum, it is readily attacked by both hydrochloric and dilute sulphuric acids, owing to the formation of a galvanic couple (p. 297, also footnote, p. 296). For this reason impure commercial zinc gives hydrogen very rapidly. Zinc and hot concentrated sulphuric acid give zinc sulphate, sulphur dioxide, and water. Zinc also dissolves chemically in a hot concentrated solution of sodium hydroxide, sodium zincate and hydrogen being slowly formed,

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Finely divided zinc (commercial zinc-dust, p. 624, which generally contains a little zinc oxide), in conjunction with a dilute acid or a solution of sodium hydroxide, is used as a reducing agent; zinc-dust is also employed as a paint for iron-work.

Zinc, like magnesium, is a bivalent metal. Its salts are derived from the oxide ZnO, and the soluble ones are prepared by treating the metal or the oxide with the required acid. All the compounds described below are colourless.

Zinc oxide, ZnO, is prepared by heating the carbonate or nitrate, but may also be obtained from the hydroxide, and by burning the metal. It turns yellow when heated, but loses its colour again when cooled. It is insoluble in water, but dissolves chemically in nearly all acids. It is used as a paint (*zinc-white*).

Zinc hydroxide, $Zn(OH)_2$, is obtained as a white precipitate when a solution of a zinc salt is treated with sodium hydroxide or ammonium hydroxide, but the precipitate dissolves on an excess of either of these reagents being added; in the case of sodium hydroxide this is due to the formation of a soluble zincate, in which the zinc hydroxide plays the part of an acid,

$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O,$$

but in the case of ammonium hydroxide a more complex action occurs.

Zinc chloride, $ZnCl_2$, is prepared by treating scrap zinc with hydrochloric acid and then evaporating the solution until it solidifies when cooled. The product, which is often cast into sticks, is not pure, but contains basic zinc chloride, which is formed by the hydrolysis of the normal salt,

$$ZnCl_2 + H_2O = ZnCl{\cdot}OH + HCl.$$

Pure anhydrous zinc chloride is prepared by strongly heating a mixture of zinc sulphate and sodium chloride, when zinc chloride (b.p. 730°) distils, leaving a residue of sodium sulphate.

Zinc chloride is colourless, hygroscopic, and very readily soluble in water. It is used in soldering on account of its property of dissolving metallic oxides; it is also used in protecting wood from the attacks of moulds or bacteria.

Zinc chloride absorbs ammonia, with which it forms several compounds, as, for example, $ZnCl_2, NH_3$.

Zinc sulphate, $ZnSO_4, 7H_2O$ (p. 226), formed, together with the oxide, when zinc sulphide is roasted (in the air); like magnesium sulphate, it forms double salts of the type $ZnSO_4{\cdot}X_2SO_4, 6H_2O$ (p. 491).

Zinc carbonate, $ZnCO_3$, like magnesium carbonate, is insoluble in water, but it undergoes hydrolysis, so that the substance obtained by precipitation is a basic carbonate or a mixture of carbonate and hydroxide.

Zinc sulphide, ZnS, differs from magnesium sulphide in not being hydrolysed by water. It is obtained as a colourless precipitate when ammonium sulphide solution is added to a solution of a zinc salt,

$$ZnCl_2 + (NH_4)_2S = ZnS + 2NH_4Cl ;$$

but it is not precipitated when hydrogen sulphide is passed through such a solution (p. 220). It dissolves chemically in hydrochloric acid, but is insoluble in acetic acid in presence of acetates: this last fact is made use of in separating zinc from manganese in analytical work.

CADMIUM, Cd; AT. WT. 112·4.

Cadmium is very similar to zinc in most respects, and is of relatively small importance; the metal is used in making fusible alloys (p. 569), and its sulphide is used as a paint.

Cadmium occurs in the same states of combination as zinc, and is obtained in the way already described (p. 624). In order to free it from zinc it is converted into cadmium chloride and then into cadmium sulphide (see below); the metal is again obtained from the sulphide by roasting the latter and then reducing the oxide with coal.

Cadmium has a bright silvery lustre and a sp. gr. of about 8·6; it melts at about 320° and boils at about 780°. Its behaviour towards acids resembles that of zinc.

Cadmium oxide, CdO, is brown; the colourless **hydroxide**, $Cd(OH)_2$, is insoluble in a solution of sodium hydroxide, but dissolves chemically in ammonium hydroxide solution. The **chloride**, $CdCl_2, 2H_2O$, is not hygroscopic and is not hydrolysed by water. The **sulphate**, $3CdSO_4, 8H_2O$, differs from zinc sulphate as regards water of hydration, and is not of the vitriol type. The **carbonate**, $CdCO_3$, is not hydrolysed by water.

All the above-named compounds are prepared by methods similar to those used in obtaining the corresponding derivatives of zinc; except the oxide, they are all colourless.

Cadmium sulphide, CdS, is obtained as an orange-yellow precipitate when hydrogen sulphide is passed through a solution of a cadmium salt,

$$CdSO_4 + H_2S = CdS + H_2SO_4.$$

It is insoluble in dilute hydrochloric or sulphuric acid, and is therefore precipitated under conditions which do not allow of the formation of zinc sulphide.

MERCURY, Hg; AT. WT. 200.

Mercury, the only metal which is liquid at ordinary temperatures, is found in small quantities in the free state, but it occurs principally in the form of its sulphide, HgS, a dull-red mineral known as *cinnabar* (p. 221), which is mined at Almaden in Spain, in Austria, Russia, Mexico, California, and other places.

The conversion of mercuric sulphide into mercury and sulphur dioxide is easily accomplished by heating the compound in an oxidising atmosphere,

$$HgS + O_2 = Hg + SO_2;$$

and on the large scale this change is brought about in furnaces of various kinds. The mercury volatilises, together with sulphur dioxide and furnace gases, and the principal difficulty lies in condensing the mercury vapour, for which purpose the products are passed through long flues.

The crude metal may be freed from dust and dross by filtering it through chamois leather, but it still contains small quantities of lead, copper, and other elements; such impure samples tarnish on exposure to the air, owing to the oxidation of the impurities, and adhere to the surface of glass; they also leave a 'tail' of oxide or dross in a vessel from which they have been poured.

Pure mercury is obtained either by distilling the crude metal from iron retorts, or by treating it with very dilute nitric acid; in the latter case, the acid converts the dissolved impurities into soluble salts, and the mercury is subsequently washed with water.

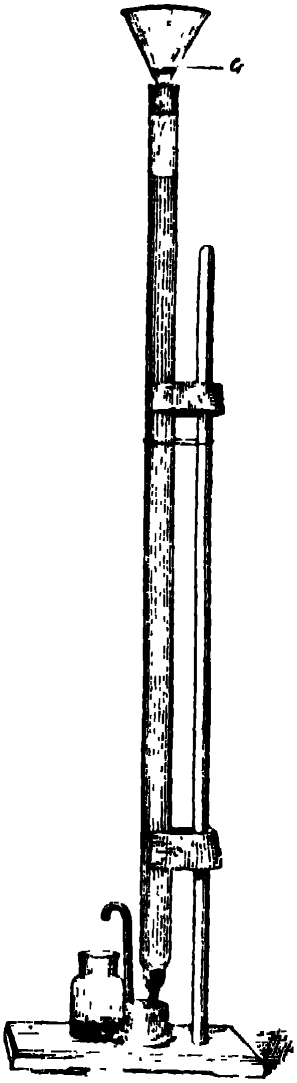

Fig. 114.

A form of apparatus used in the laboratory for the purification of mercury is shown in fig. 114. The metal escapes from the funnel (*a*) in a very fine stream, and overflows into the receiver.

When pure mercury is dissolved in hot nitric acid, and the solution is evaporated to dryness, the salt thus obtained leaves no residue when it is ignited; if, however, the mercury contains iron, lead, copper, &c., these impurities remain as non-volatile oxides.

Mercury is a silvery liquid of sp. gr. 13·6; it crystallises (and melts) at −39·4° and boils at 357°. The density of the vapour is *about* 100; hence the molecular weight of mercury is *about* 200. Now, as the atomic weight of mercury is 200, it follows that the molecule of mercury is *monatomic* (p. 383)—that is to say, consists of only *one* atom; the molecular formula, therefore, is Hg. Cadmium and zinc and many other metals are also monatomic.

Mercury is used in the construction of thermometers, barometers, pumps, and other physical apparatus; in working with gases which are soluble in water; in the extraction of silver and gold from their ores; and in making mirrors. It has the property of dissolving many other metals, and forming with them mixtures or compounds which are termed *amalgams*.

Amalgams may be prepared by simply adding a metal to mercury at ordinary temperatures, or by heating the two metals together; also in some cases by covering mercury with a salt of a metal. Thus, when mercury is left in contact with a solution of silver nitrate the silver is displaced by mercury,

$$AgNO_3 + Hg = HgNO_3 + Ag,$$

and then dissolves in the excess of the latter.

A tin-mercury amalgam was formerly used in making mirrors, but nowadays silver is principally employed; sodium amalgam (p. 670) is of some importance.

Mercury does not change on exposure to the air at ordinary temperatures, but at about 300° it is slowly converted into mercuric oxide. It is not attacked by hydrochloric acid or by dilute sulphuric acid to an appreciable extent, but with hot concentrated sulphuric acid it gives a sulphate of the metal, with evolution of sulphur dioxide,

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

Nitric acid acts on mercury fairly rapidly, unless the acid is cold and very dilute, and with excess of nitric acid mercuric nitrate is formed, with evolution of nitric oxide (p. 243),

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O.$$

Mercury, unlike magnesium, zinc, and cadmium, gives rise to *two* basic oxides, namely, *mercurous oxide*, Hg_2O, and *mercuric oxide*, HgO. The salts derived from mercurous oxide are not actually prepared from this oxide, and excepting mercurous chloride and mercurous nitrate, are not of much importance; they probably contain *uni*valent mercury. The salts derived from mercuric oxide contain *bi*valent mercury, and are of the same type as the corresponding salts of magnesium, zinc, and cadmium.

Mercuric nitrate, $Hg(NO_3)_2$, is formed when mercury is heated with excess of moderately concentrated nitric acid (see above), and is obtained in colourless crystals when the solution is evaporated. It is readily soluble in dilute nitric acid, but it is hydrolysed by water, giving an insoluble basic salt,

$$Hg(NO_3)_2 + H_2O = Hg(NO_3) \cdot OH + HNO_3,$$

the composition of which depends on the conditions; when this basic salt is boiled with excess of water it is completely hydrolysed and mercuric oxide is formed.

Mercuric nitrate decomposes when it is gently heated, giving a residue of scarlet mercuric oxide, which at higher temperatures is converted into mercury and oxygen (footnote, p. 237).

Mercuric oxide, HgO, may be obtained by cautiously heating the nitrate, or, more economically, by heating a mixture of mercuric nitrate and mercury. It is also obtained by treating a solution of a mercuric salt with a solution of sodium hydroxide,

$$Hg(NO_3)_2 + 2NaOH = HgO + 2NaNO_3 + H_2O;$$

in this latter reaction, the hydroxide, $Hg(OH)_2$, which may be the first product, is not obtained, as it does not exist at ordinary temperatures.

Mercuric oxide prepared by precipitation is yellow and amorphous, and quite different in physical properties from the red crystalline substance obtained by heating the nitrate. Both varieties are insoluble in water, and with acids give the mercuric salts; they both turn dark brown when they are heated (p. 81).

Mercuric sulphate, $HgSO_4$, is prepared by heating the metal with concentrated sulphuric acid; it is crystalline, and is converted into an insoluble basic salt when it is treated with water.

Mercuric chloride, $HgCl_2$, may be obtained by dissolving the oxide in hot moderately concentrated hydrochloric acid, and then concentrating the (filtered) solution until long, needle-shaped crystals begin to separate. On the large scale the salt is prepared by heating an intimate mixture of mercuric sulphate and sodium chloride,

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4;$$

the mercuric chloride sublimes and condenses to a colourless crystalline mass, the non-volatile sodium sulphate remaining behind.

Mercuric chloride melts at 265° and boils at 307°; its vapour density corresponds with that required by the molecular formula $HgCl_2$. It is readily soluble in hot water, and, like all soluble mercury salts, it is exceedingly poisonous; it is employed in preserving wood, and in extremely dilute solution it is used as an antiseptic. From its properties it is commonly known as *corrosive sublimate*.

An aqueous solution of mercuric chloride gives with ammonium hydroxide a colourless precipitate (commonly known as '*white precipitate*') of *mercuri-ammonium chloride*,

$$HgCl_2 + 2NH_3 = NH_2{\cdot}HgCl + NH_4Cl.$$

This preparation is used in medicine. It may be regarded as derived from ammonia by displacing one atom of hydrogen by the univalent group of atoms $-HgCl$, or from mercuric chloride by displacing one atom of chlorine by the univalent amino-group $-NH_2$.

Mercuric iodide, HgI_2, like several other well-known mercury compounds, exists in two forms. It is obtained as a scarlet insoluble precipitate on a mercuric salt being treated with potassium iodide in aqueous solution, but the iodide must be added cautiously, as the precipitate combines with potassium iodide to form a colourless soluble compound, $HgI_2, 2KI$, or K_2HgI_4. This scarlet form of mercuric iodide changes at 126°, more rapidly at 150-200°, into a canary-yellow form, which melts at 223° and volatilises at higher temperatures; the yellow form, when cooled again to ordinary temperatures, may remain unchanged, but when rubbed or when touched with a particle of the scarlet modification it changes into the latter. This behaviour of mercuric iodide is analogous to that of sulphur and of many other solids which exist in physically different (polymorphous) forms.

Nessler's solution is prepared by adding potassium iodide to mercuric chloride, both in aqueous solution, until the precipitated mercuric iodide has been converted into the soluble complex salt (p. 591) **potassium mercuric iodide,** K_2HgI_4 (see above), and then rendering the solution strongly alkaline with potassium hydroxide. This solution gives with ammonia or with any ammonium salt a yellowish-brown precipitate,

$$2HgI_2 + 4NH_3 = NHg_2I + 3NH_4I,$$

and even with traces of ammonia a yellow or brown colouration is obtained; hence Nessler's solution is employed in testing drinking-waters for contamination with sewage.

Mercuric sulphide, HgS, is obtained as a black precipitate when hydrogen sulphide is bubbled through a solution of a mercuric salt,

$$HgCl_2 + H_2S = HgS + 2HCl;$$

but the first product is generally a colourless precipitate of the composition $HgCl_2, 2HgS$, which changes first to yellow and then to black as it passes into the sulphide.

Mercuric sulphide is also formed, together with mercury, when hydrogen sulphide is passed into a solution of a mercurous salt; the reason of this is that mercurous sulphide, the initial product, undergoes decomposition at ordinary temperatures,

$$2HgNO_3 + H_2S = Hg_2S + 2HNO_3$$
$$Hg_2S = HgS + Hg.$$

The black form of mercuric sulphide, obtained by precipitation, sublimes when it is heated out of contact with the air, and gives a dark lustrous crystalline sublimate; this product closely resembles native cinnabar, and gives a scarlet powder when it is ground. The black sulphide also passes slowly into the red form when it is left in contact with a solution of sodium sulphide. The two varieties of mercuric sulphide have the same composition, and like the two mercuric iodides are different physical forms of one and the same compound. The scarlet sulphide is used as a paint (vermilion), in colouring sealing-wax, &c.

Mercuric sulphide is insoluble in hydrochloric acid and in nitric acid, but with aqua regia (p. 236) it gives soluble mercuric chloride; as already stated, it is converted into mercury and sulphur dioxide when it is heated in the air.

Mercurous nitrate, $HgNO_3$, is formed when mercury is left in contact with cold dilute nitric acid, and is obtained in colourless hydrated crystals, $HgNO_3, H_2O$, on the solution being evaporated. It is hydrolysed by water, giving an insoluble basic salt, $Hg(OH), HgNO_3$, and its solution in dilute nitric acid undergoes oxidation on exposure to the air,

$$4HgNO_3 + 4HNO_3 + O_2 = 4Hg(NO_3)_2 + 2H_2O.$$

In view of the latter fact a little mercury is generally kept in solutions of mercurous nitrate, as the metal reduces any mercuric nitrate which may be formed,

$$Hg(NO_3)_2 + Hg = 2HgNO_3.$$

Mercurous oxide, Hg_2O, is obtained as a black precipitate on mercurous nitrate being treated with sodium hydroxide in aqueous solution; the hydroxide, $Hg(OH)$, is unknown,

$$2HgNO_3 + 2NaOH = Hg_2O + H_2O + 2NaNO_3.$$

Mercurous oxide decomposes when it is gently heated, giving mercuric oxide and mercury; the same decomposition occurs when the oxide is treated with acids, and in consequence a mercuric salt is formed under these conditions as the result of a secondary reaction.

Mercurous chloride, $HgCl$, is insoluble in water, and is obtained as a colourless precipitate on mercurous nitrate being treated with hydrochloric acid in aqueous solution,

$$HgNO_3 + HCl = HgCl + HNO_3.$$

It is prepared on a large scale by heating mercuric chloride with mercury, or by heating mercuric sulphate with mercury and sodium chloride,

$$HgSO_4 + Hg + 2NaCl = 2HgCl + Na_2SO_4.$$

The product sublimes and condenses as a colourless crystalline mass.

Mercurous chloride is decomposed by boiling hydrochloric acid, giving a solution of mercuric chloride and a residue of mercury. With nitric acid it gives a solution of mercuric chloride and mercuric nitrate.

Mercurous chloride gives with ammonium hydroxide a black product, which is probably a mixture of mercury and mercuri-ammonium chloride (p. 632),

$$2HgCl + 2NH_3 = HgNH_2Cl + Hg + NH_4Cl.$$

On account of this property mercurous chloride is commonly known as *calomel* (from a Greek word meaning 'fine black').

Mercurous chloride is used in medicine; for this purpose it must be most carefully freed from the more highly poisonous mercuric salt by extracting the latter with water. It is met with in qualitative analysis (*a*) in separating mercurous or univalent mercury from other metals, and (*b*) in testing for mercuric chloride with stannous chloride, or *vice versâ* (p. 590).

In absence of every trace of water, pure mercurous chloride gives a vapour the density of which (at 448°) corresponds with that required by the formula Hg_2Cl_2. In presence of moisture the vapour density is only half that of the perfectly dry vapour, but under these conditions the salt dissociates into mercury and mercuric chloride. It is doubtful whether the existence of the molecules, Hg_2Cl_2, should be regarded as a case of association or as evidence that mercury is bivalent in this compound.

Mercurous iodide, HgI, is not very stable. It seems to be formed as a yellowish green solid when iodine is rubbed with excess of mercury or when mercurous nitrate is treated with potassium iodide in aqueous solution, but it decomposes in sunlight, giving a mixture of mercury and mercuric iodide.

THE RELATIONSHIP BETWEEN THE ELEMENTS OF THE MAGNESIUM FAMILY.

Of the elements included in this family, magnesium, zinc, and cadmium are more closely related to one another than they are to mercury; the last-named metal is exceptional in forming an oxide, X_2O, and a series of corresponding salts in which the element is apparently univalent, and in which it shows some relationship to the members of the copper family (p. 665). The mercurous derivatives being excluded, it will be seen that the members of the magnesium family all give rise to compounds in which the metals are *bivalent* —as, for example, the oxides XO, the hydroxides $X(OH)_2$, and the chlorides XCl_2; corresponding compounds resemble one another in physical and in chemical properties, and show, as in other cases, a gradual change in properties in passing from the derivatives of magnesium to those of mercury.

Since magnesium is almost as closely related to the members of the calcium family as to zinc, cadmium, and mercury, the further consideration of these analogies may be deferred until the calcium family has been dealt with.

CHAPTER LVIII.

The Calcium Family.

The three elements, calcium, strontium, and barium, which constitute this family are very closely related. They occur in nature chiefly in the form of their carbonates and sulphates, which are white earthy minerals; their carbonates are 'mild alkalis' (p. 75), while their hydroxides resemble in many respects those of the alkali-metals, and are 'caustic alkalis' (p. 75). For these reasons calcium, strontium, and barium are often spoken of as the metals of the *alkali-earths*.

CALCIUM, Ca; AT. WT. 40·1.

The more important naturally occurring compounds of calcium have already been fully described (pp. 57–62, 69–75, 226, 401, 549), and also certain compounds, such as calcium oxide (quicklime, p. 57), calcium hydroxide (slaked lime, p. 58), and calcium chloride (p. 148), which are obtained from these minerals. Calcium compounds are contained in all animals and plants (p. 139).

The free element is now manufactured by the electrolysis of the fused anhydrous chloride, a process by which it was first obtained by Davy.

As thus produced it has the appearance of lead, but is much harder than the latter, and is cut only with difficulty; its sp. gr. is about 1·85 (or 1·5), and its melting-point about 760°. It is a very active metal; like magnesium it burns when it is heated in the air, giving calcium oxide and some *calcium nitride*, Ca_3N_2. It decomposes water readily, with formation of calcium hydroxide and liberation of hydrogen,

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

It combines with nitrogen at a red heat, and also gives compounds with hydrogen,* sulphur, phosphorus, carbon, and other elements; the nitride (see above) is decomposed by water, giving ammonia and calcium hydroxide.

Calcium is sometimes used in separating small quantities of water from alcohols.

Calcium carbide, CaC_2, is manufactured by heating a mixture of coal and limestone at a very high temperature in an electric furnace; the calcium oxide produced from the limestone reacts with the carbon of the coal, giving calcium carbide and carbon monoxide,

$$CaO + 3C = CaC_2 + CO.$$

The liquid product solidifies on cooling to a gray, very hard, crystalline mass, which is used for the preparation of acetylene,

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2,$$

and for other purposes (p. 519).

The salts of calcium are derived from the oxide CaO. The insoluble ones, such as the carbonate, phosphate, and fluoride, and the sparingly soluble sulphate, are all natural minerals and are not manufactured; in the laboratory they may be obtained by precipitation. The soluble calcium salts are prepared by dissolving the native carbonate in acids; but as limestone often contains impurities, pure calcium carbonate must be used in the laboratory if pure preparations are required.

Calcium oxide, CaO, prepared by heating the carbonate, nitrate, or hydroxide of calcium, is colourless, and only melts at the highest temperature of the electric furnace. In the impure form (quicklime, p. 57) it is used in generating the lime-light (p. 135), and also as a lining for crucibles and furnaces.

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* **Calcium hydride,** CaH_2 (known commercially as hydrolith), is rapidly formed when calcium is heated in dry hydrogen; when placed in water it gives hydrogen and calcium hydroxide.

Calcium hydroxide, $Ca(OH)_2$, prepared by slaking quicklime (p. 58), is used in the manufacture of ammonia (p. 267), caustic soda (p. 672), and bleaching-powder, in making mortar and cements,* in tanning, and in agriculture; its aqueous solution, lime-water, is used in softening natural waters (p. 281) and in medicine.

Calcium chloride, $CaCl_2$, has already been described (p. 148);† the **bromide**, $CaBr_2$, and the **iodide**, CaI_2, resemble the chloride; but the fluoride is almost insoluble in water.

Bleaching-powder is a very important commercial product obtained by passing chlorine into chambers the floors of which are covered with a layer of dry slaked lime.

The chambers are made of flag-stones luted together with asphalt, or else of sheet lead. At first the chlorine is rapidly absorbed, and care must be taken that the temperature does not rise above 30°, otherwise some calcium chlorate is formed. When the absorption of the gas is at an end, the bleaching-powder is packed into casks.

The change which occurs during the conversion of slaked lime into bleaching-powder consists essentially in the transformation of calcium hydroxide into calcium hypochlorite and calcium chloride,

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O,$$

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* Ordinary *mortar*, a mixture of wet slaked lime and sand, gradually hardens on exposure to the air owing to the formation of calcium carbonate, which is slowly deposited around the particles of sand, and then gradually becomes crystalline.

Hydraulic cements, such as Portland cement, which harden under water, are prepared by cautiously heating carefully prepared, finely divided mixtures of limestone or chalk and clay. When the product is mixed with water to a paste it rapidly hardens, even under water, owing probably to the hydration of the calcium and aluminium silicates. (Compare p. 227.)

† The hydrated salt, $CaCl_2, 6H_2O$, dissolves in water with absorption of heat. The anhydrous salt absorbs ammonia, forming a compound, $CaCl_2, 8NH_3$.

a reaction which has already been studied (p. 430). It would seem, however, that a secondary reaction also takes place, whereby the chloride and hypochlorite react to form a salt which is partly a chloride and partly a hypochlorite,

$$CaCl_2 + Ca(OCl)_2 = 2CaCl(OCl) \text{ or } 2Ca\!<\!\begin{matrix}Cl\\ OCl\end{matrix},$$

and which, therefore, may be called **calcium chlorohypochlorite.**

The principal reasons for believing that this secondary change occurs are: (*a*) bleaching-powder is not hygroscopic, (*b*) alcohol does not extract soluble matter from it. As calcium chloride is very hygroscopic and is soluble in alcohol, its presence in bleaching-powder is very unlikely. Possibly the interaction of chlorine and slaked lime takes place in the two stages represented by the following equations,

$$Ca(OH)_2 + Cl_2 = CaCl(OH) + HOCl$$
$$CaCl(OH) + HOCl = CaCl(OCl) + H_2O.$$

When bleaching-powder is treated with cold water it gives a strongly alkaline solution, but it does not dissolve completely in, say, 50 times its own weight of water; the insoluble matter consists principally of calcium hydroxide.

These facts seem to show that bleaching-powder contains calcium hydroxide, and no doubt samples which have not been thoroughly chlorinated do so. Well-prepared samples, however, are probably almost free from calcium hydroxide, and this substance is only formed as the result of the hydrolysis of calcium hypochlorite,

$$Ca(OCl)_2 + 2H_2O \longleftrightarrow Ca(OH)_2 + 2HOCl,$$

produced from the calcium chlorohypochlorite when the latter is treated with water,

$$2CaCl(OCl) = Ca(OCl)_2 + CaCl_2.$$

The aqueous solution of bleaching-powder, like the dry powder, has a smell recalling that of chlorine and that of hypochlorous acid; this solution is used in commercial bleaching.

When a coloured material—as, for example, blotting-paper soaked in litmus solution—is placed underneath the surface of a solution of bleaching-powder, the coloured substance is only very slowly attacked; if, however, the material is first dipped into the bleaching-powder solution and then exposed to the air, it is bleached much more rapidly, and even more quickly still when exposed to carbon dioxide. This is because the calcium chlorohypochlorite is relatively stable, but when it is treated with (atmospheric) carbonic acid it gives hypochlorous acid (p. 431), which is a vigorous oxidising (bleaching) agent.

Bleaching-powder gives chlorine when it is treated with hydrochloric or sulphuric acid,

$$CaCl(OCl) + 2HCl = Cl_2 + CaCl_2 + H_2O$$
$$CaCl(OCl) + H_2SO_4 = Cl_2 + CaSO_4 + H_2O.$$

The quantity of chlorine which is thus obtained depends on that of the calcium chlorohypochlorite contained in the sample and not on the nature of the acid. In these reactions hypochlorous acid is first liberated; in the case of hydrochloric acid the changes may be expressed thus:

$$CaCl(OCl) + HCl = CaCl_2 + HOCl$$
$$HOCl + HCl = Cl_2 + H_2O,$$

and in the case of sulphuric acid thus:

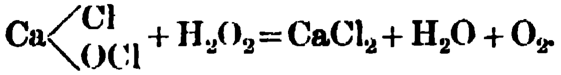
$$CaCl(OCl) + H_2SO_4 = CaSO_4 + HCl + HClO$$
$$HOCl + HCl = Cl_2 + H_2O.$$

The bleaching-power thus depends on the quantity of hypochlorous acid given by the sample, because it is this acid which *oxidises* the colouring matters, and is itself reduced to hydrogen chloride. As, moreover, the quantity of chlorine which is liberated by acids also depends on that of the hypochlorous acid (see equations), it follows that the bleaching value of a sample of the powder may be ascertained by finding the percentage of chlorine given by the powder when it is mixed with excess of an acid.

This is very easily done by treating a known weight of the sample with acetic acid * in presence of excess of potassium iodide, and then finding how much iodine has been liberated by titration with sodium thiosulphate (p. 497). The quantity of chlorine thus determined is usually about 36–38 per cent. in good samples of the powder. This chlorine is termed *available chlorine.*

If bleaching-powder were a pure compound of the composition $CaCl(OCl), H_2O$, produced in accordance with the equation already given (p. 639), it would contain 49 per cent. of available chlorine, but even the very best samples contain only 42-43 per cent.

The available chlorine may also be determined by treating the powder with excess of hydrogen peroxide in a nitrometer (p. 476) and measuring the liberated oxygen,



$$Ca\begin{cases}Cl\\OCl\end{cases} + H_2O_2 = CaCl_2 + H_2O + O_2.$$

Bleaching-powder deteriorates when it is kept, especially if exposed to light, and in strong sunlight oxygen is liberated, sometimes very rapidly.

Other hypochlorites, prepared by electrolysis (p. 432), are now being used as substitutes for bleaching-powder.

Calcium nitrate, $Ca(NO_3)_2$, prepared by treating the carbonate with nitric acid, is obtained in colourless hydrated crystals ($4H_2O$) on evaporating the solution; it shows the usual behaviour of a metallic nitrate when it is heated,

$$2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2.$$

Calcium sulphate, $CaSO_4$ (pp. 226, 281), and calcium phosphate, $Ca_3(PO_4)_2$ (p. 549), have been described. The sulphate dissolves chemically in moderately concentrated hydrochloric acid, owing to the occurrence of the reversible reaction,

$$CaSO_4 + 2HCl \longleftrightarrow CaCl_2 + H_2SO_4,$$

and the phosphate behaves in a similar manner,

$$Ca_3(PO_4)_2 + 6HCl \longleftrightarrow 3CaCl_2 + 2H_3PO_4;$$

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* Acetic acid is used because stronger acids would act on any *chlorate* present, liberating chlorine; as the chlorate is useless for bleaching purposes, the chlorine obtained from it by the action of strong acids is not available chlorine.

but if the solutions are evaporated hydrochloric acid volatilises and the reactions proceed from right to left (p. 359).

Calcium sulphide, CaS, is formed when an intimate mixture of calcium sulphate and charcoal is strongly heated out of contact with the air,

$$CaSO_4 + 4C = CaS + 4CO,$$

but the product cannot be purified; it is practically insoluble in water (p. 274), but in contact with water it is slowly hydrolysed, giving calcium hydroxide and soluble calcium hydrosulphide,

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2.$$

For this reason calcium hydrosulphide, and not calcium sulphide, is formed when hydrogen sulphide is passed into a solution of calcium hydroxide,

$$Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O.$$

Volatile calcium salts, such as the chloride, give a red colour to a non-luminous flame.

STRONTIUM, Sr; AT. WT. 87·6.

The metal strontium is so very closely related to calcium that a very brief description of its compounds will suffice, especially as few of these are of any great importance. The naturally occurring strontium compounds are the carbonate, $SrCO_3$, which is found as the mineral *strontianite*, and the sulphate, $SrSO_4$, which is often of a blue colour, and is hence known as *celestine*.

Strontium may be obtained by the electrolysis of fused strontium chloride, but the free element (sp. gr. about 2·5) is practically unknown; it resembles calcium, but is rather more active than the latter

The soluble salts of strontium are easily prepared from the carbonate, but they cannot be directly obtained from the sulphate, as this compound is practically insoluble in acids. When the sulphate is used as a source of strontium compounds it is first reduced to the *sulphide*, SrS, by heating it with coal or pitch; the sulphide is then transformed into the chloride or nitrate (dilute acid being used).

Strontium oxide, SrO, is obtained by heating the nitrate or the hydroxide; it cannot be conveniently prepared from the carbonate as this salt decomposes only at very high temperatures. The oxide resembles calcium oxide, and combines with water to form the hydroxide.

Strontium hydroxide, $Sr(OH)_2$, is perhaps the most important strontium compound from a practical standpoint. It is manufactured by passing superheated steam over the heated carbonate,

$$SrCO_3 + H_2O = Sr(OH)_2 + CO_2.$$

This (reversible) change is brought about more readily than the dissociation of the carbonate, partly because the steam rapidly removes the liberated carbon dioxide, partly because the combination of the oxide with water is an exothermic reaction.

Strontium hydroxide is not decomposed by heat so readily as is calcium hydroxide, and it is more soluble in water than the latter; from its solutions it separates in hydrated crystals, $Sr(OH)_2, 8H_2O$.

When the hydroxide is added to a solution of (impure) cane-sugar (sucrose), it gives with the sugar an insoluble precipitate of strontium sucrosate; for this reason the hydroxide is used in preparing pure sugar from molasses (treacle) and other impure samples. The precipitated sucrosate is separated from the mother-liquor, which contains the impurities, and is then suspended in water and treated with carbon dioxide; it is thereby decomposed, giving a precipitate of insoluble strontium carbonate, and a solution of pure sucrose, which is afterwards evaporated.

Strontium chloride, $SrCl_2$, and **strontium nitrate,** $Sr(NO_3)_2$, are readily soluble in water.

Strontium carbonate, $SrCO_3$, is insoluble in water and may be obtained by precipitation,

$$SrCl_2 + (NH_4)_2CO_3 = SrCO_3 + 2NH_4Cl.$$

Like calcium carbonate, it dissolves chemically in carbonic acid, giving the soluble but unstable ***strontium hydrogen carbonate***, $Sr(HCO_3)_2$.

Strontium sulphate, $SrSO_4$, may be converted into other strontium compounds in the manner described (p. 643), and also (in the laboratory) by the following process: The finely powdered sulphate is mixed with about five or six times its weight of 'fusion mixture,'* and the mixture is strongly heated over the blowpipe-flame in a platinum crucible. After the product is cooled, it is boiled with water in order to dissolve the sulphates of sodium and potassium which have been formed,

$$SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4.$$

The insoluble strontium carbonate is then separated by filtration, washed with water until free from soluble sulphates, and finally dissolved in the required acid. It should be noted that if the product of fusion is directly treated with an acid (before the soluble sulphates have been removed), the strontium salt which is formed immediately reacts with the soluble sulphate, and insoluble strontium sulphate is regenerated.

Strontium salts, which volatilise when heated in the Bunsen-flame, impart to the flame a crimson colouration

BARIUM, Ba; AT. WT. 137·4.

Barium, like strontium and calcium, occurs in nature in the form of its carbonate, $BaCO_3$, and sulphate, $BaSO_4$. The former is found as the mineral *witherite*, the latter as the mineral *heavy spar* or *barytes* (sp. gr. 4·4), both of which are colourless and crystalline.

Barium may be obtained by the electrolysis of fused barium chloride; its chemical properties are similar to those of strontium and calcium, but it is even more active than strontium.

*** A mixture of the carbonates of sodium and potassium which melts more easily than does sodium carbonate alone.**

The derivatives of barium are prepared from its naturally occurring compounds by methods similar to those used in obtaining strontium derivatives from strontianite and celestine. Thus, from witherite, barium chloride and barium nitrate may be directly prepared; but as heavy spar, the more abundant mineral, is insoluble in acids, it is first converted into the sulphide by heating it with coal or pitch (p. 643).

The sulphate may also be heated with pitch and calcium chloride; when the sulphate has been reduced to sulphide the mass is extracted with water, the solution is separated from the insoluble calcium sulphide which is formed,

$$BaS + CaCl_2 = BaCl_2 + CaS,$$

and the barium chloride is obtained in crystals by concentrating and then cooling the solution.

Barium monoxide, BaO, cannot be conveniently prepared by heating barium hydroxide or barium carbonate, because so high a temperature is required to decompose these compounds.

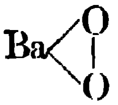
Barium carbonate may be converted into the oxide by heating it with coal dust at about 1450° during an hour or so; the carbon of the coal hastens the decomposition, because it reacts with the carbon dioxide to form carbon monoxide, and thus diminishes the molecular concentration of the former.

It is usually prepared by strongly heating barium nitrate, but even this decomposition is not easily accomplished in the laboratory.

Barium monoxide is colourless; when heated in oxygen, or in purified air, at about 500° it is converted into the dioxide. It combines readily with water, forming the hydroxide.

Barium hydroxide, $Ba(OH)_2$, is more readily soluble than strontium hydroxide, and separates from saturated aqueous solutions in lustrous hydrated crystals, $Ba(OH)_2, 8H_2O$; it is a strong base, and its aqueous solution (*baryta-water*) absorbs carbon dioxide very readily, the insoluble carbonate being precipitated.

Barium peroxide, BaO_2, may be obtained by the method mentioned above, but the pure oxide is best prepared by treating a concentrated solution of barium hydroxide with a fairly concentrated solution of hydrogen peroxide. The hydrated crystals, $BaO_2, 8H_2O$, which are then precipitated, may be dehydrated by cautiously warming them in a vacuum.*

Barium peroxide or dioxide is an important compound, and is used in the manufacture of oxygen (and hydrogen peroxide). It is not a basic oxide, since with acids it gives salts derived from barium monoxide; its constitution may be represented by one of the following formulæ,  or $Ba=O=O$, but it is difficult to decide between them.

The only important soluble salts of barium are the chloride and the nitrate, which are prepared by the methods given above.

Barium chloride, $BaCl_2$, is less readily soluble in water than is strontium chloride, and separates from aqueous solutions in hydrated crystals, $BaCl_2, 2H_2O$; **barium nitrate,** $Ba(NO_3)_2$, is anhydrous.

Barium carbonate, $BaCO_3$, as already stated, is much more stable towards heat than is calcium carbonate; it may be prepared in a pure state by precipitation, as it is not hydrolysed by water.

Barium sulphate, $BaSO_4$, is also obtained in a pure state by precipitation, and is the least soluble of all the sulphates. It is slowly and only incompletely converted into carbonate when it is boiled with a concentrated aqueous solution of sodium carbonate (p. 360), and it is not appreciably soluble in acids. In order to prepare other compounds from barium sulphate in the laboratory, the salt is heated with excess of fusion mixture, and the product is then treated in the manner described in the case of strontium sulphate (p. 645), care being taken to extract all the sodium sulphate with water *before* adding an acid to the barium carbonate.

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* Hydrated crystals of strontium dioxide and of calcium dioxide may be obtained from strontium and calcium hydroxides respectively in a similar manner.

That barium sulphate may be practically completely converted into the carbonate by fusing it with about 4 gram-molecules of fusion mixture is probably due to the separation of the carbonate from the fused mixture of salts as the latter cools, and before the sulphate begins to crystallise out.

Barium sulphate is employed as a paint (*permanent white*) and as a 'filling' in making writing-paper, &c.

Other barium salts insoluble in water are the **chromate,** $BaCrO_4$, and the **phosphate,** $Ba_3(PO_4)_2$.

Barium sulphide, BaS, like calcium sulphide, is hydrolysed by water, giving the soluble hydrosulphide and hydroxide,

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2.$$

Volatile barium compounds, such as the chloride, impart a yellowish-green colour to a Bunsen-flame.

THE RELATIONSHIP OF THE ELEMENTS OF THE CALCIUM FAMILY.

The similarity between the three *bivalent* metals of this family is so striking that it is hardly necessary to discuss their relationship. Their oxides, XO, hydroxides, $X(OH)_2$, chlorides, XCl_2, carbonates, XCO_3, sulphates, XSO_4, and, in fact, all their corresponding compounds have similar physical and chemical properties. At the same time there is a gradual change in these properties in passing from calcium through strontium to barium, whether the elements themselves are considered, or any series of corresponding derivatives. The nature of this change is in most cases expressed by saying that the basic character of the element becomes more pronounced as the atomic weight increases. Barium is more vigorous than strontium, and strontium than calcium, in its action on water. Barium hydroxide is more soluble, more active, and more stable towards heat than calcium hydroxide, and strontium hydroxide stands between the two. Similarly, barium carbonate is more stable towards heat than calcium carbonate, while strontium carbonate has intermediate properties. In these and in other respects barium approaches more nearly the alkali metals than does strontium, while calcium forms a connecting link with the members of the magnesium family.

The elements of the magnesium sub-family *and* those of the calcium sub-family constitute Family II. of the periodic system (p. 720). The family being taken as a whole, it may be said that the anomalies are few in number, while the regularities are well marked. Beryllium and magnesium may be regarded as belonging equally to both sub-families; while they differ from zinc, cadmium, and mercury in being 'light metals,' in giving sulphides which are decomposed by water, and in other respects, they also differ from calcium, strontium, and barium in giving hydroxides which are almost insoluble in water, in giving carbonates which are converted into oxides at comparatively low temperatures, and so on. Differences such as these are only to be expected, since a 'break' is often observed in passing from elements of the small to those of the large periods.

The typical compounds of Family II. are those in which the elements are bivalent, and the close chemical relationship shown by corresponding compounds has already been indicated. Further examples of the gradual change in properties with increasing atomic weight are given in discussing the periodic system (p. 724).

The exceptional or 'abnormal' behaviour of mercury in giving rise to the mercur*ous* derivatives has already been noted. Even if it is assumed that mercury is bivalent in these compounds—and the evidence for or against this view is not very conclusive—the other elements of the family do not form corresponding derivatives.

CHAPTER LIX.

The Metals of the Copper Family.

Three well-known metals are included in this family, namely, copper, silver, and gold These elements have the ordinary physical characteristics of heavy metals, and they are all very good conductors of electricity. In their chemical behaviour they are not very closely related, for although they are all univalent in certain of their compounds and thus give rise to compounds of the same type, copper is bivalent in its best-known salts, and gold is tervalent. There is, therefore, a wide difference between these derivatives of univalent silver, bivalent copper, and tervalent gold.

COPPER, Cu; AT. WT. 63·6

This metal occurs in nature in the free state, and in consequence has been known from the very earliest times; it derives its name from Cyprus, whence it was at one time principally obtained. Large quantities of native copper are now mined in the neighbourhood of Lake Superior, in Chili, Peru, and Bolivia, and occasionally large masses weighing as much as 450 tons are found; sometimes the metal occurs in crystals.

Many compounds of copper are also found in nature, and most of the world's supply of the metal is obtained from these compounds. The oxide, Cu_2O, occurs as the mineral *cuprite* or *red copper ore*. Basic carbonates are represented by *malachite*, $CuCO_3, Cu(OH)_2$, and *azurite*, $2CuCO_3, Cu(OH)_2$; the former is a green, beautifully veined stone which is often used for ornamental work, while the latter has a deep-blue colour. Cuprous sulphide, Cu_2S, is found as *copper glance*, and, mixed with sulphides and arsenides of iron and other metals, as *copper pyrites*, Cu_2S, Fe_2S_3 (or $CuFeS_2$).

Owing to the great variety of the ores of copper and the many different copper compounds which they contain, in addition to sand, clay, calcium silicate, &c., the extraction of the metal is not an easy matter, and various processes are employed; moreover, the different ores may be introduced at different stages of the operations.

The principles on which these processes are based are as follows:

When sulphide ores are roasted in a (reverberatory) furnace the sulphides of iron, zinc, and other metals are oxidised, with formation of a metallic oxide and liberation of sulphur dioxide, but the cuprous sulphide remains practically unchanged. On the heat being increased, the metallic oxides unite with the silica present, forming a fusible slag, and the cuprous sulphide also melts. These two liquid products separate from one another, and the cuprous sulphide is run off from below.

When the cuprous sulphide, freed from other sulphides, is now heated in a reverberatory furnace it gradually undergoes oxidation,

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2,$$

and after some time a mixture of oxide and sulphide results.

On the heat being then increased, the cuprous oxide which has been formed reacts with the unchanged sulphide (compare lead, p. 593), and copper is produced, with liberation of sulphur dioxide,

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

In the process which is principally employed in England the following operations are carried out:

(1, *a*) *Roasting for Coarse Metal.* The sulphide ores, and the slags from 2, *b*, are roasted in a reverberatory furnace (fig. 110, p. 587). The iron pyrites and arsenical pyrites are thus oxidised, and sulphur dioxide and arsenious anhydride volatilise, but the changes are incomplete.

(1, *b*) *Melting for Coarse Metal.*—The temperature is raised, whereupon the oxides of iron unite with the silica and clay to form a fusible slag. Any cuprous or cupric oxide which has been formed reacts with sulphide of iron,

$$Cu_2O + FeS = Cu_2S + FeO$$
$$2CuO + 2FeS = Cu_2S + 2FeO + S,$$

and the oxide of iron thus formed passes into the slag. The slag and the cuprous sulphide separate into two liquid layers, and the cuprous sulphide is run out into water in order to granulate it. The impure cuprous sulphide thus obtained is called *coarse metal.*

(2, *a*) *Roasting for Fine Metal.* This stage is a repetition of 1, *a*, and the object is to eliminate sulphur and arsenic as before.

(2, *b*) *Melting for Fine Metal.*– This stage is a repetition of 1, *b*, but the cuprous sulphide which is now obtained is far richer than before, and is called *fine metal.*

(3, *a*) *Roasting for Blister Copper.*—The cuprous sulphide (fine metal) is heated in an oxidising atmosphere in order to convert some of the sulphide into oxide (see p. 651); oxide ores, free from sulphur compounds, are sometimes added to the fine metal.

(3, *b*) *Melting for Blister Copper.*—The mixture of oxide and sulphide is strongly heated in order to bring about the interaction shown above (p. 651); during this operation the escaping sulphur dioxide often carries away fine particles of copper which are deposited in the flues (copper-rain). The liquid metal is run off. The name blister copper is given to it because the sulphur dioxide which continues to escape during the cooling of the metal causes blisters or bubbles at the surface.

The slags, rich in copper, resulting from this last operation are worked up again with the coarse metal from 1, *b*.

The copper resulting from these operations generally contains about 98 or 99 per cent. of this metal and small quantities of many others (silver, lead, nickel, iron), as well as combined oxygen, arsenic, and sulphur. As even very small quantities of impurities affect its properties (more especially its electrical conductivity) the metal has next to be refined.

For this purpose the blocks or ingots of crude copper are piled on the hearth of a reverberatory furnace and gently heated in an oxidising atmosphere for some hours; sulphur and arsenic are then expelled as oxides, the changes being assisted by the porous character of the ingots; the foreign metals present and some of the copper are also oxidised. The metal is next melted, skimmed until free from slag, and then covered with anthracite (coal), or wood charcoal, in order to bring about the reduction of dissolved oxides of copper; this reduction is also accomplished by stirring the metal with wooden poles (*'poling'*). Samples of the purified metal are examined from time to time; and when, judging by its physical properties, it is at the right *'pitch,'* it is taken out in iron ladles lined with clay and cast into ingots.

Copper is also refined by an electrolytic process. The crude metal is cast into slabs, which are suspended in a solution of copper sulphate acidified with sulphuric acid; in close proximity to these slabs, thin sheets of pure copper are also suspended. An electric current is then passed through the solution from the copper slabs, which are connected with the anode, to the thin sheets, which are connected with the cathode. The copper passes into solution and the pure metal is deposited on the sheets; the impurities also dissolve, but they either remain in solution or separate as a deposit, which collects at the bottom of the vessel. The process is carried out in a wooden vat which is lined with sheet-lead. Copper which has been refined electrolytically is almost free from impurities, and many contain as much as 99·99 per cent. of the pure element.

Copper has a characteristic salmon-red lustre, which, however, varies a little with the physical condition of the metal. It is very tough, ductile, and malleable. Its sp. gr. is about 8·95, and it melts at about 1060°. On long exposure to the air it becomes coated with a layer of basic carbonate, and when heated in the air it undergoes rapid oxidation, giving first cuprous and then cupric oxide; it does not decompose water even at a red heat. As copper is a very good conductor of electricity it is very extensively employed for that purpose; it is also used in the manufacture of various utensils, for covering roofs and the hulls of ships, for the preparation of a great many important alloys, and also for making copper salts, especially the sulphate.

Copper does not give good castings, as it is liable to become porous when used for such purposes; many of its alloys, however, especially the various qualities of *brass*, not only cast well but are more easily worked than copper itself.

The more important copper alloys are *brass* (copper and zinc) and *bronze* (copper and tin), of each of which there are several varieties.

Brass contains variable proportions of copper (70–64 per cent.) and zinc (30–36 per cent.), and is prepared by adding zinc to molten copper. Alloys containing about 15 per cent. of zinc are called *tombac*; those with about 20 per cent. of zinc have a golden colour, and are used for ornamental purposes and in making imitation gold-leaf; those with about 40–50 per cent. of zinc are known as *Muntz metal.*

Bronze contains variable proportions of copper and tin, and often relatively small quantities of other elements as well. *Gun-metal* consists of about 90 per cent. of copper and 10 per cent of tin; *bell-metal*, of about 78 per cent. of copper and 22 per cent. of tin. Bronze used for ornamental purposes generally contains a small proportion of lead and zinc. The important alloy *phosphor-bronze* contains about 90 per cent. of copper, 9·5 per cent. of tin, and 0·5 per cent. of phosphorus. The British bronze coins consist of copper, 95; tin, 4; and zinc, 1, per cent.

Copper is rapidly attacked by ordinary nitric acid, giving copper nitrate, water, and nitric oxide (compare p. 245), or some other oxide of nitrogen (p. 530). Hydrochloric acid and dilute sulphuric acid do not act on the metal to any appreciable extent; but in presence of (atmospheric) oxygen they both do so, especially when they are hot, and a copper salt passes into solution,

$$2Cu + 4HCl + O_2 = 2CuCl_2 + 2H_2O$$
$$2Cu + 2H_2SO_4 + O_2 = 2CuSO_4 + 2H_2O.$$

Even acetic acid and other 'weak' acids have an action on the metal in presence of oxygen, and a basic acetate of copper is prepared by leaving copper in contact with vinegar

(p. 279) and air; this product is also known as *verdigris*, and is used in making green paints.

The action of hot concentrated sulphuric acid on copper has been described (p. 230).

Copper forms two basic oxides, namely, *cuprous oxide*, Cu_2O, and *cupric oxide*, CuO. The salts derived from cupric oxide may be directly prepared from this compound; but cuprous oxide when treated with acids gives a cupric salt together with copper, so that the cuprous salts have to be prepared by other methods. In its cuprous compounds, copper is probably univalent – that is to say, the structure of the oxide is probably $Cu-O-Cu$; but in its cupric compounds it is bivalent, and the cupric salts are therefore of the same type as those of the bivalent metals of the magnesium family.

For the preparation of the oxides and salts of copper in the laboratory commercial copper sulphate may be employed, or the metal may be converted into its nitrate, and this salt used instead.

CUPRIC OXIDE AND THE CUPRIC SALTS.

Cupric oxide, CuO, may be obtained by igniting copper nitrate (p. 43), copper carbonate, or copper hydroxide;* it is a black powder, and is readily reduced to the metal when it is heated in a stream of coal-gas (p. 44), hydrogen (p. 109), or carbon monoxide (p. 121), or with carbon compounds (p. 123). It is used in the analysis of carbon compounds and for the preparation of copper salts.

Cupric hydroxide, $Cu(OH)_2$, is formed as a blue precipitate when a solution of sodium hydroxide is added to a solution of copper sulphate or other cupric salt. Ammonium hydroxide likewise gives this precipitate; but as cupric hydroxide and ammonium hydroxide react and form a soluble compound, the precipitate disappears again on excess of ammonium hydroxide being added, and a beautiful deep-blue solution is obtained. When the blue, precipitated hydroxide is heated in presence of water it is partially changed into oxide and turns black; it is completely converted into the oxide when it is ignited.

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* The word 'copper' is often used instead of 'cupric' in the case of the cupric salts.

Cupric chloride, $CuCl_2$, may be obtained by heating copper in excess of chlorine, or by heating the metal with hydrochloric acid and a little nitric acid, but more conveniently by treating the oxide or hydroxide with hydrochloric acid and then evaporating the (filtered) solution. It forms blue hydrated crystals, $CuCl_2$, $2H_2O$, but the anhydrous salt is dark yellowish-brown.

Cupric bromide, $CuBr_2$, is known, but **cupric iodide** does not exist (p. 658).

Cupric nitrate (copper nitrate) has been described (p. 43). **Cupric carbonate** is not known in a pure state; the precipitate obtained on sodium carbonate being added to a copper salt in aqueous solution (p. 45) is a *basic carbonate*, $CuCO_3$, $Cu(OH)_2$.*

Cupric sulphate, $CuSO_4$, is colourless (p. 36); but the hydrated salt, $CuSO_4$, $5H_2O$ (p. 225), is of a deep-blue colour. This salt is prepared commercially for agricultural purposes (p. 225); it is also used in dyeing, in electrolytic work (copper-plating), and in batteries.

Cupric sulphide, CuS, is obtained as a black precipitate when hydrogen sulphide is passed into a solution of a cupric salt, but it is not very stable, and decomposes partially, giving *cuprous sulphide* and sulphur; this change takes place completely when cupric sulphide is heated out of contact with the air (to prevent oxidation). Cupric sulphide is not readily attacked by hydrochloric acid, but with nitric acid it gives cupric nitrate.

Fehling's solution is the name given to a deep-blue solution prepared by dissolving blue vitriol (34·6 g.) and sodium potassium tartrate* (173 g.) in water, then adding sodium hydroxide (60 g.), and diluting the mixture to 1000 c.c. This solution contains a (soluble) compound produced by the interaction of the tartrate and cupric hydroxide; this copper compound is readily reduced to cuprous oxide by various sugars and other carbon compounds, and Fehling's solution is used as a qualitative and quantitative reagent in the examination of such substances.

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* Compare p. 511.

CUPROUS OXIDE AND THE CUPROUS SALTS.

Cuprous oxide, Cu_2O, is obtained as a brick-red precipitate when Fehling's solution is added to a boiling solution of grape-sugar (glucose). It is acted on by acids, but as a rule it gives a cupr*ic* salt and copper,

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

It gives with ammonium hydroxide a colourless solution which rapidly absorbs oxygen.

Cuprous hydroxide is not known in a pure state.

Cuprous chloride, $CuCl$, is conveniently prepared by heating copper turnings with a solution of cupric chloride in hydrochloric acid,

$$CuCl_2 + Cu = 2CuCl;$$

on the (filtered) solution being poured into a large volume of water the cuprous chloride is precipitated in colourless crystals.

Another method is to pass sulphur dioxide into a solution of equivalent quantities of copper sulphate and sodium chloride; the sulphurous acid reduces the cupric chloride which is formed by the reversible reaction,

$$CuSO_4 + 2NaCl \longleftrightarrow CuCl_2 + Na_2SO_4,$$

and converts it into insoluble cuprous chloride,

$$2CuCl_2 + H_2SO_3 + H_2O = 2CuCl + 2HCl + H_2SO_4.$$

As the concentration of the cupric chloride is thus continuously reduced, the above reversible reaction proceeds continuously from left to right.

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* The hydrated salt, $NaKC_4H_4O_6, 4H_2O$, commonly known as Rochelle salt.

Cuprous chloride is insoluble in water, but it is hydrolysed by boiling water, giving cuprous oxide and hydrochloric acid. With hydrochloric acid it forms soluble compounds ($HCuCl_2$ and H_2CuCl_3). The solution obtained by treating cuprous chloride with concentrated hydrochloric acid or with ammonium hydroxide absorbs and combines with carbon monoxide, and is used for extracting this compound from gaseous mixtures in the process of gas analysis.

Cuprous iodide, CuI, is precipitated when an iodide and a cupric salt are mixed together in aqueous solution; the cupric iodide, which is probably first produced by double decomposition, $CuSO_4 + 2KI = K_2SO_4 + CuI_2$, is unstable, and gives cuprous iodide and iodine,

$$2CuI_2 = 2CuI + I_2;$$

the final results being,

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI + I_2.$$

The iodide is almost colourless and insoluble in water

The above reactions may be used for the estimation of copper, and also for separating iodides from bromides and chlorides (p. 428), since cupric bromide and cupric chloride do not give cuprous salt and halogen under such conditions.

Cuprous sulphide, Cu_2S, has already been mentioned (p. 656).

The cuprous salts and most of the anhydrous cupric salts are either colourless or yellow or brown, but the hydrated cupric salts and their aqueous solutions are generally blue or green. The cuprous salts are readily oxidised to the cupric compounds

Volatile copper compounds impart a green colour to a non-luminous flame.

SILVER, Ag; AT. WT. 107·9.

This metal is found in nature in the free state, generally associated with a small proportion of gold, and also in the form of various compounds, of which *argentite* or *silver glance*, Ag_2S, and *chlorargyrite* or *horn-silver*, $AgCl$, may be mentioned; the occurrence of a small proportion of silver sulphide in galena has already been noted.

A considerable quantity of silver is obtained from argentiferous lead in the manner previously described (p. 594), also by smelting silver ores with lead ores, and then extracting the silver by Pattinson's or Parke's method.

In localities where fuel is expensive the Mexican amalgamation process is used. The ore is stamped or ground to a paste with water, and is then agitated with common salt; after some days copper sulphate is added, the mixture is again agitated, and lastly it is thoroughly incorporated with mercury for a period of some weeks or even months. As the result of a number of chemical changes the silver is liberated from its compounds and is dissolved by the mercury; the liquid amalgam is finally freed from earthy matter by washing it with water, and the mercury is then separated from the silver by distillation. Some of the chemical changes are probably represented by the following equations:

$$2NaCl + CuSO_4 = CuCl_2 + Na_2SO_4$$
$$Ag_2S + CuCl_2 = 2AgCl + CuS$$
$$2AgCl + Hg = HgCl_2 + 2Ag.$$

The sodium chloride solution dissolves the silver chloride, and thus facilitates the action of the mercury.

Silver obtained by heating some of its compounds—as, for example, the oxide—is white and dull, and it may be obtained by precipitation as a black powder. Its ordinary appearance is familiar to all. It has a sp. gr. of about 10·5, and melts at about 960°. The principal uses of silver are for the manufacture of utensils, ornaments, and coins, and for coating other metals and glass. As the pure metal is not very hard, silver coins and other articles are composed of silver-copper alloys. Thus the British coinage contains 7·5 per cent. of copper, and is said to be of a fineness of 925 (because it contains 925 parts of silver per 1000 of the alloy). The proportion of copper in the alloys used for other purposes may be much greater.

Silver does not change on exposure to the atmosphere except in or near places where coal is burnt; in such localities it is acted on by the traces of hydrogen sulphide present in the atmosphere, and its surface is darkened owing to the formation of a film of silver sulphide.

The so-called 'oxidised silver' is prepared for ornamental purposes by dipping the silver object in a solution of potassium sulphide; the surface is then rubbed or brushed in order to shade it.

Although molten silver does not *combine* with oxygen, it has the very interesting property of absorbing or dissolving this gas; when the metal is kept melted in the air, it gradually absorbs about 24 times its own volume of oxygen, and if then allowed to cool it gives up the gas again almost completely. During the cooling, and after a semi-solid layer has been produced at the surface of the metal, the escape of the oxygen causes the formation of little 'volcanoes' from which the still molten metal is ejected in thin streams. This phenomenon is known as the 'spitting' of silver.

Silver is readily attacked by warm diluted nitric acid (p. 238), and also by boiling concentrated sulphuric acid,

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O,$$

but it is not acted on by hydrochloric acid. When heated in chlorine it is transformed into silver chloride, and when heated with sulphur or hydrogen sulphide it is converted into silver sulphide (p. 219).

Silver forms the basic oxide, Ag_2O, and the silver salts correspond with this oxide, in which the metal is univalent. The starting-point for the preparation of most silver compounds is the silver nitrate of commerce, which is itself prepared from the metal (p. 238).

Silver oxide, Ag_2O, is obtained as a pale-brown precipitate, probably mixed with silver hydroxide, $AgOH$, when a solution of sodium hydroxide is added to a solution of a silver salt. Before the precipitate has been dried it is appreciably soluble in cold water, giving a solution which is distinctly alkaline to litmus, and which, therefore, probably contains the *hydroxide*; but in any case this hydroxide readily passes into the oxide, and the dried precipitate has the composition represented by Ag_2O. Silver oxide, like the oxides of mercury, gold, and platinum, is readily decomposed into metal and oxygen, and when heated at about 270° it gives a residue of (white) silver.

Silver oxide gives with ammonium hydroxide a soluble compound, of undetermined composition, which is obtained as a black solid when the solution is allowed to evaporate; this solid is dangerously explosive, even when it is moist, and is known as *fulminating silver.* The solution of this compound is generally known as 'an ammoniacal solution of silver oxide.'

Silver oxide is easily reduced by various carbon compounds such as grape-sugar (glucose), tartrates, glycerol, and formaldehyde, and from the solution of silver oxide in ammonium hydroxide (see above) the metal may be deposited on glass surfaces in a coherent, highly lustrous form. In silvering glass for mirrors, &c., a solution of silver nitrate is treated with sufficient ammonium hydroxide to redissolve the precipitated oxide of silver, one of the above reducing agents is added, and the mixture is then poured over the carefully cleaned glass surface which is to be silvered.

Silver peroxide, Ag_2O_2, is formed by the action of ozone on silver (p. 462); it is not a salt-forming oxide, and its structure may be represented by the formula $Ag-O-O-Ag$.

Silver nitrate, $AgNO_3$ (pp. 238, 242), **silver chloride,** $AgCl$ (p. 148), **silver sulphate,** Ag_2SO_4 (p. 224), **silver sulphide,** Ag_2S (p. 219), and many other silver salts, have been described; but the haloid compounds are of great importance, and merit further mention.

Although *silver fluoride,* AgF, is soluble in water, the *chloride,* $AgCl$, *bromide,* $AgBr$, and *iodide,* AgI, are insoluble, and may therefore be prepared by precipitation. The chloride is thus obtained as a colourless, the bromide as a very pale-yellow, and the iodide as a pale-yellow, curdy substance; the chloride and bromide darken on exposure to light (p. 662).

The insolubility of the chloride, bromide, and iodide in water and in nitric acid renders these substances suitable not only for the *detection*, but also for the *estimation* of the halogen acids and their salts, as fully described in the case of silver chloride (p. 149).

Although insoluble in water, these three compounds are readily transformed into various soluble derivatives; when they are treated with sodium thiosulphate (p. 498) or potassium cyanide (p. 679), for example, in aqueous solution, they pass into soluble compounds represented by the formulæ $NaAgS_2O_3$ and $KAg(CN)_2$ respectively.

With ammonium hydroxide silver chloride reacts to form a readily soluble compound; so also (but not so readily) does the bromide; the iodide is practically insoluble in ammonium hydroxide.

The silver halides, which darken on exposure to light, but more especially the *bromide*, are used in *photography*, the darkening is probably due to the formation of a sub-halogen salt, such as Ag_2Br.

Silver may be obtained again from the insoluble chloride, bromide, or iodide by leaving these compounds in contact with zinc and dilute sulphuric acid; the halide is reduced by the 'nascent' hydrogen (p. 341), and the halogen acid thus formed,

$$Zn + H_2SO_4 + 2AgCl = ZnSO_4 + 2HCl + 2Ag,$$

does not act on the liberated metal.* This process is used in removing these silver salts from crucibles in which they have been melted in the course of quantitative analysis; also for the preparation of *pure* silver.

Silver may also be obtained from these halogen compounds by boiling them with sodium hydroxide solution and cane-sugar; the halide is reduced, and silver is obtained as a dark powder.

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* The very finely divided silver thus obtained is much more active than the compact metal, and is known as '*molecular silver*.'

GOLD, Au; AT. WT. 197·2.

This relatively rare and beautiful metal is found almost exclusively in the free state, but never in a pure condition; it often contains a considerable proportion of silver. It occurs in grains, crystals, or large masses, in veins of quartz, or in the sand produced by the disintegration of the rock components.

It is also found in very small quantities in iron pyrites, arsenical pyrites, and many other minerals which contain sulphides, also in combination with tellurium (p. 500).

The primitive method of extracting gold was to agitate the crushed rock, or the sand, with water, in such a manner that the lighter earthy materials were washed away, leaving the heavier particles of gold. Later on, the rich sediment obtained in this way was shaken with mercury, which dissolved the gold, forming a liquid amalgam; the latter, which could be easily separated from the sludge, was then heated in order to volatilise the mercury.

At the present day the gold-bearing rocks are stamped by machinery, and the material is then carried in the form of a paste or sludge by a stream of water over copper plates which are coated with mercury; a certain proportion of the gold is thus extracted, and the mercury amalgam scraped from the plates is then heated in iron retorts in order to distil and recover the mercury and separate the gold. The material ('tailings') which has thus been extracted, and also very poor ores, are treated by the *cyanide process*. Gold is acted on by an aqueous solution of potassium cyanide (p. 679) in presence of atmospheric oxygen, giving soluble *potassium aurocyanide*,

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH;$$

the ores are therefore extracted with a dilute (say 0·5 per cent.) solution of potassium cyanide in huge wooden vats, and the gold is then obtained from the solution either by depositing it electrolytically on leaden electrodes, or by precipitating it with zinc.

Another method of extracting gold, particularly from ores containing metallic sulphides, is to roast the crushed ore in order to expel sulphur (as sulphur dioxide), and then to treat the product with bleaching-powder and dilute sulphuric acid (or with chlorine and water). The gold is converted into soluble auric chloride, and the solution of this compound is then treated with ferrous sulphate, which precipitates the gold as a reddish-brown powder,

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

The crude gold obtained by any of these methods may be purified by passing chlorine through the melted metal; many of those metals which are present in small quantity are thus converted into *volatile* chlorides, while the chloride of silver which is produced forms a non-volatile layer at the surface of the melted mass. Gold, at its melting-point, does not combine with chlorine.

Gold is very malleable and can be beaten out into extremely thin sheets (gold-leaf), which are often so thin (less than 0·0002mm.) as to be transparent to green light. It melts at about 1060°, and has a sp. gr. of 19·3. As pure gold is relatively soft, the metal used for making coins and for nearly all other purposes is alloyed with copper. The British gold coins contain 2 parts by weight of copper in 24 parts of the alloy, and consist of what is called '22-carat' gold (the pure metal is 24-carat). The alloys used in making gold-ware may be either 22, 18, 15, 12, or 9-carat gold.

Gold is not attacked by hydrochloric, nitric, or sulphuric acid, but when treated with aqua regia (p. 236) it is converted into soluble auric chloride; it is also readily acted on by moist chlorine at ordinary temperatures, and by an aqueous solution of potassium cyanide in presence of oxygen (p. 663).

Gold forms two series of compounds: the *aurous* compounds, in which the metal is univalent, and the *auric* compounds, in which it is tervalent. The former correspond with the cuprous compounds and with the derivatives of silver, but the auric salts are more commonly met with.

Auric chloride, $AuCl_3$, is produced when gold is treated with aqua regia; on the yellow solution being evaporated, yellow hydrated crystals of *chlorauric acid*, $AuCl_3, HCl$, or $HAuCl_4$, remain; and when this substance is very cautiously heated it decomposes, giving auric chloride, $AuCl_3$, a red crystalline salt. On potassium chloride being added to auric chloride in concentrated aqueous solution, **potassium aurichloride**, $KAuCl_4, 2H_2O$, is obtained in yellow crystals.

Hydrated yellow crystals of **ammonium aurichloride**, $(NH_4)AuCl_4$, may be obtained from ammonium chloride in a similar manner. **Sodium aurichloride**, $NaAuCl_4, 2H_2O$, is used in photography.

Auric hydroxide, $Au(OH)_3$, is precipitated as a yellowish brown solid when a solution of auric chloride is treated with a basic hydroxide, but it is an acid, and is converted by excess of the basic hydroxide into a metallic *metaurate*; with sodium hydroxide, for example, soluble **sodium metaurate**, $NaAuO_2$, is formed, the normal acid, $Au(OH)_3$, giving $HO{\cdot}AuO$ and H_2O. When ammonium hydroxide is added to a solution of auric chloride, a greenish-brown, highly explosive substance (*fulminating gold*) is precipitated.

Aurous chloride, $AuCl$, is obtained when auric chloride is heated at about 180°. It is a colourless solid, insoluble in water, and when heated strongly it is decomposed into its elements. **Aurous oxide**, Au_2O, is obtained as a brownish-violet powder by treating aurous chloride with sodium hydroxide solution.

As already noted, the relationship between copper, silver, and gold is not a very close one. In physical properties they resemble one another in being very good conductors of heat and of electricity, in which respects they surpass all other metals. In chemical properties the resemblance is limited to those compounds in which the elements are univalent. They all form basic oxides of the type X_2O and chlorides of the type XCl. These chlorides are all colourless and insoluble in water, but with ammonium hydroxide, sodium thiosulphate, and several other compounds, they yield corresponding derivatives which are readily soluble.

Copper differs from the other two elements in giving rise to stable, well-defined compounds in which it is bivalent. These compounds show in many respects a fairly close relationship with corresponding derivatives of the bivalent elements of the magnesium and calcium sub-families, and also with corresponding derivatives of iron, cobalt, nickel, and manganese. This fact affords a further instance of the general rule that the properties of a compound depend on the type of that compound rather than on the elements of which it is composed.

Gold differs from the other two elements of the sub-family in forming compounds in which it is tervalent, and in which it shows some relationship to aluminium and other members of Family III.

CHAPTER LX.

The Alkali Metals.

The meaning of the term 'alkali' has already been explained (p. 75), and it has also been stated that the caustic alkali, sodium hydroxide, NaOH, was obtained long ago by treating an aqueous solution of the mild alkali, sodium carbonate, with milk of lime. In 1807 it was found by Davy that sodium hydroxide could be decomposed with the aid of a current of electricity (see p. 668), and that it was a compound of an element to which the name *sodium* was given. In a similar manner potassium hydroxide, KOH, was found to be a compound of an element to which the name potassium was given.* These elements, obtained from alkalis, and subsequently found to have the properties of metals, were classed as the *alkali metals*. In later times three other metals (lithium, rubidium, and cæsium) having properties similar to those of sodium and potassium were discovered, and the natural family of the alkali metals now consists of these five elements.

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* The symbol of sodium, Na, is derived from *Natrium*, the German name for sodium, which is derived from *natron*, a word of Arabian origin. The symbol of potassium, K, is derived from Kalium (German), which is also of Arabian origin (*alkali*, the ash).

Lithium, Li, at. wt. 7·0, occurs in a combined state in many plants (notably in the tobacco-plant), but only in very minute quantities. Traces of its compounds are also found in some natural waters and in many rocks. It is a silvery solid, and is the lightest metal known, its sp.gr. being only 0·53. Its general behaviour is very similar to that of sodium, from which it differs principally in giving a hydroxide, LiOH, a carbonate, Li_2CO_3, and a phosphate, $2Li_3PO_4, H_2O$, which are far less soluble in water than the corresponding sodium compounds. The carbonate and the phosphate may be obtained from a solution of the chloride, LiCl, by precipitation; the former is used in medicine in cases of gout and rheumatism, because *lithium urate* is more soluble in water than most other salts of uric acid, and it is (or was) supposed that the administration of lithium carbonate would assist the elimination from the system of the deposits of uric acid which are formed in such cases.

SODIUM, Na; AT. WT. 23·0.

Sodium is by far the most abundant of the alkali metals. It occurs only in the combined state in the form of sodium salts. Sodium silicate is a component of many igneous rocks, and occurs in some minerals (as, for example, in albite, p. 291) in considerable quantities. In the course of ages the sodium silicate, liberated by the disintegration of such rocks, passes into solution, and is changed into other soluble sodium salts, such as the chloride, carbonate, nitrate, and sulphate, by interaction with other earthy materials. In consequence of their solubility, sodium salts are present in larger or smaller quantities in all fresh waters; they are carried into lakes and seas, where they slowly accumulate (p. 112), and by the gradual evaporation of such lakes or inland seas vast beds of sodium salts have been deposited in many parts of the world. The occurrence of sodium chloride in such deposits (as rock-salt) and in sea-water has already been noted, and the way in which sodium nitrate is produced has also been indicated (p. 241). The sulphate (p. 226) and the carbonate (p. 273) occur principally in the dissolved state.

Sodium compounds are also contained in plants (particularly in those growing in or near the sea) and in animals.

Sodium is now prepared on the large scale by the electrolysis of melted sodium hydroxide. The primary products are 2Na and 2OH, but a secondary change immediately occurs at the anode, resulting in the liberation of oxygen and the formation of water. Owing to the presence of this water, and to water originally contained in the hydroxide, the fused mass also gives, to some extent, the products of electrolysis of a *solution* of sodium hydroxide—namely, hydrogen and oxygen (p. 303). The final results, therefore, are the liberation of sodium and hydrogen at the negative pole and of oxygen at the positive pole.

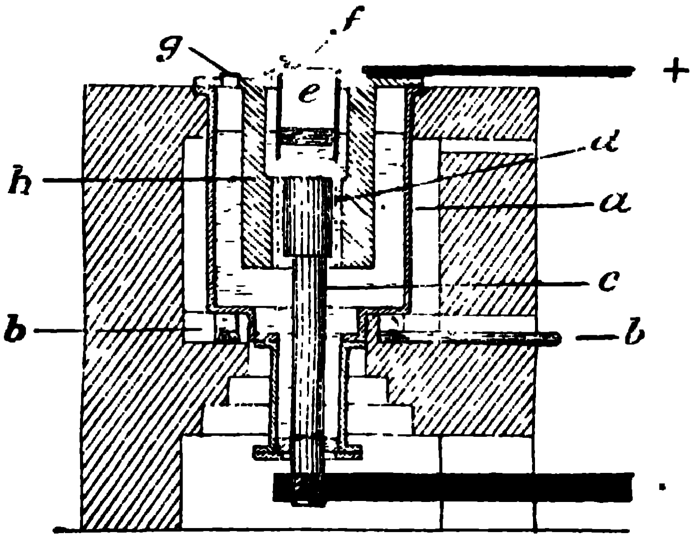

Fig. 115.

The apparatus used in this process is shown in fig. 115. The sodium hydroxide contained in the cylindrical iron vessel (*a*) is first melted with the aid of the circular gas-burner (*b*, *b*). The iron or nickel cylinder (*h*), insulated from the vessel (*a*) by means of asbestos, forms the anode, and the cylinder (*c*), also insulated, forms the cathode. The sodium and the hydrogen liberated at the surface of (*c*) rise through the fused hydroxide, and, guided by the cylinder of iron gauze (*d*), the sodium collects in the chamber (*e*), while the hydrogen escapes under the loosely fitting cover (*f*). The sodium is ladled out from time to time with finely perforated iron spoons. The oxygen liberated at the anode escapes through the aperture (*g*).

Sodium is a very soft metal, and is easily cut with a knife or pressed through a die; it has a bright metallic lustre, very like that of silver; but in other respects it does not show those physical properties which are commonly associated with the term metal. Its sp. gr. is only 0·97, and it melts at 98°. It rapidly tarnishes on exposure to the air, because it is so readily acted on by aqueous vapour; for this reason it must be kept in well-closed vessels, or, if in small pieces, immersed in petroleum. It takes fire and forms oxides when it is heated in the air, and it decomposes water with great vigour, liberating hydrogen and giving sodium hydroxide,

$$2Na + 2H_2O = H_2 + 2NaOH.$$

A violent and dangerous explosion (the cause of which is not known) often occurs when sodium and water are brought together, and the best way of studying this interaction is to wrap a small piece of the metal securely in a piece of fine iron gauze, which is then placed, with the aid of a pair of tongs, under a gas-jar filled with water standing in the pneumatic trough. A glass screen may be used as an additional precaution.

Sodium is a very active element; it combines directly with most of the non-metals either at ordinary temperatures or on the application of heat, and also acts on nearly all compounds. Thus it liberates nearly all elements from their oxides, and it displaces hydrogen from water, ammonia, hydrogen sulphide, and many other hydrogen compounds, but not as a rule from hydrocarbons (p. 125). All experiments with this metal should be very cautiously conducted.

The principal laboratory uses of sodium are for the preparation of sodium amalgam, and for testing for certain elements in organic compounds.

Sodium Amalgam.—When a piece of sodium (say about 0·5 gram) is thrown on to some mercury (say 500 g.) contained in a mortar, and is then pressed with a pestle under the mercury, the two elements combine, with development of heat, and sometimes with a flash of light.*

On the addition of sodium being continued until the product contains about 2 per cent. of the latter, and the mass being then allowed to cool, a hard, silvery solid, *sodium amalgam*, is obtained.

This amalgam is readily acted on by water with formation of hydrogen, sodium hydroxide, and mercury, but the reaction is quite a gentle one and free from danger, hence sodium amalgam is often employed in conjunction with water, or some dilute acid, as a reducing agent, its action being due to the generation of nascent hydrogen (p. 341). Thus very dilute nitric acid is reduced by sodium amalgam, and is ultimately converted into ammonia (p. 530).

When coarsely crushed sodium amalgam is added (in considerable proportion) to a concentrated aqueous solution of ammonium chloride, a bulky, silvery product of a buttery consistency is rapidly formed. This product is known as *ammonium amalgam*, and possibly contains an alloy, or a compound, of mercury with the radicle *ammonium*, (NH_4), which is unknown in the free state (p. 266). The sodium in the sodium amalgam may liberate this ammonium radicle, ($Na + NH_4Cl = NaCl + NH_4$), and the latter may then dissolve in or combine with the mercury. Whatever its nature may be, the product is very unstable, even at low temperatures, and rapidly decomposes, giving ammonia, mercury, and hydrogen.

Oxides of sodium are formed when the metal is gently heated in air which has been dried and freed from carbon dioxide; the first product is probably *sodium monoxide*, Na_2O, but as this compound combines readily with oxygen, giving *sodium peroxide*, Na_2O_2, it is not obtainable in a pure state. The *monoxide*, Na_2O, is a colourless solid, and is the only salt-forming oxide of sodium, it unites vigorously with water, giving sodium hydroxide.*

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* In order to protect the eyes from possible injury by the spirting of the materials, the mortar should be covered with a piece of cardboard, in the centre of which a hole is made for the passage of the pestle. Care should also be taken not to inhale the vaporised mercury.

Sodium peroxide, Na_2O_2, is manufactured by heating shavings of sodium on aluminium trays in a stream of dry, purified air, at about 400°. It is a pale-yellowish powder, which reacts vigorously with water, giving hydrogen peroxide and sodium hydroxide,

$$Na_2O_2 + 2H_2O = H_2O_2 + 2NaOH;$$

but at the same time, unless great care is taken to keep the solution cool, some of the hydrogen peroxide is decomposed, and a vigorous effervescence, due to the escape of oxygen, is observed.

Sodium peroxide is used, both in the dry state and in presence of water, as an oxidising agent. Thus when manganese dioxide is heated with it sodium manganate is formed (p. 450), and with chromium sesquioxide it gives sodium chromate (p. 508).

When a little alcohol is poured on a small heap of the peroxide, placed on an iron tray, the alcohol is oxidised with development of so much heat that the mixture puffs and takes fire. As many other carbon compounds, and even charcoal, are similarly acted on, sodium peroxide must not be stored in wooden cases or in paper, and when it is used as an oxidising agent in the dry state the experiment should be performed very cautiously.

The oxidising effect of sodium peroxide in presence of water may be shown by adding the powder in small quantities at a time to chromium hydroxide which is suspended in water; the green solid is transformed into sodium chromate, which passes into solution. On the large scale sodium peroxide is used as a bleaching agent.*

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* The monoxide may also be obtained in an impure condition by heating sodium with sodium nitrate.

The structure or constitution of sodium peroxide is probably similar to that of hydrogen peroxide (p. 475), and, therefore, is not yet established.

Sodium hydroxide, NaOH, commonly known as caustic soda (p. 78), is prepared on the large scale by treating an aqueous solution of sodium carbonate with milk of lime,

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

The precipitated calcium carbonate is separated by filtration, and the solution is then evaporated in iron pans until the liquid solidifies when cooled.

The above reaction is reversible, and for this reason the concentration of the sodium hydroxide solution must not exceed a certain limit, otherwise the decomposition is very incomplete.

Sodium hydroxide is also prepared from sodium chloride by electrolytic processes. Many different methods are employed, but in most of them one of the principal difficulties to be overcome is the keeping apart of the products of electrolysis; unless this is done hypochlorites and chlorates are formed (pp. 432, 435), instead of sodium hydroxide and chlorine, when electrolysis is carried out in aqueous solution.

In one process *fused* sodium chloride, resting on a layer of molten lead, is submitted to electrolysis. The anode consists of a number of graphite rods which dip into the fused sodium chloride, and at the surface of which *chlorine* is liberated. The molten lead forms the cathode and dissolves the liberated

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* It is also sold in a compact form (obtained by melting it), under the name of 'oxone,' for generating oxygen. The most convenient way of using sodium peroxide for the generation of oxygen is to mix it with about an equal weight of hydrated sodium sulphate or sodium carbonate; on this mixture being gently heated, the peroxide reacts with the water of hydration of the salt, and a steady stream of oxygen of a high degree of purity is obtained.

sodium. The molten alloy thus formed is blown by a steam-jet into a second vessel, in which the *sodium hydroxide*, produced (together with hydrogen) by the action of the steam, separates in the fused state from the molten lead; the latter is forced back into the electrolytic cell, so that the process is continuous.

In other processes an aqueous solution of sodium chloride is employed, and in some of these the cathode is a layer of mercury at the bottom of the cell. The mercury, which dissolves the sodium, is in constant circulation, and is first passed into another vessel (or another compartment) which contains water. Here the sodium amalgam reacts with the water, forming *sodium hydroxide* and *hydrogen*, and the mercury is then returned to the electrolytic cell. The anode consists of graphite rods, at the surface of which *chlorine* is liberated.

In other processes the anode (consisting of plates of black oxide of iron) and the cathode (consisting of iron plates) dip into a solution of sodium chloride, but are separated by a diaphragm of porous cement. *Chlorine* is liberated at the anode, *hydrogen* at the cathode, and the solution of *sodium hydroxide* which is formed around the cathode (p. 303) is prevented by the diaphragm from diffusing into the anode compartment.

The chlorine obtained under the above conditions is used for the manufacture of bleaching-powder and other substances, and is also sold, compressed to a liquid, in iron cylinders. The hydrogen is also compressed into cylinders and utilised for various purposes, such as for filling balloons and air-ships, for generating the oxy-hydrogen flame, &c. Further, the hydrogen may be combined with the chlorine; the hydrogen chloride thus obtained is free from impurity, except a little dissolved chlorine.

Commercial sodium hydroxide, especially that prepared from sodium carbonate which has been manufactured by the Leblanc process (p. 274), is highly impure and contains many sodium salts. It may be purified by treating it with alcohol, in which sodium hydroxide is soluble whereas the sodium salts are insoluble; the clear solution is then *decanted* and evaporated. As the hydroxide attacks glass and porcelain vessels, especially when it is hot, giving soluble sodium silicate and sodium aluminate (p. 613), these operations must be conducted in silver vessels. A better method of preparation is to dissolve pure sodium in pure methyl alcohol (p. 127) in a silver basin; the solution is then diluted with distilled water and evaporated out of contact with atmospheric carbon dioxide.

Some of the properties of sodium hydroxide have already been described (p. 78). It acts readily on the halogens (p. 430) and on colourless phosphorus (p. 541); when hot it attacks sulphur, giving sodium sulphide and sulphur dioxide,

$$3S + 4NaOH = 2Na_2S + SO_2 + 2H_2O,$$

but the latter immediately reacts with the hydroxide to form sodium sulphite, which then unites with sulphur to form sodium thiosulphate (p. 496). These three reactions are summarised in the following equation,

$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O.$$

Sodium hydroxide also acts on silicon; it attacks aluminium rapidly and zinc slowly, giving hydrogen and a sodium salt of the metallic hydroxide (which acts as an acid).

From solutions of metallic salts, sodium hydroxide precipitates those hydroxides which are insoluble, or only sparingly soluble, in water—as, for example, the hydroxides of manganese, chromium, tin, lead, aluminium, zinc, cadmium, copper, magnesium. In those cases in which the hydroxide is unstable (mercury, silver) the oxide of the metal is precipitated. As many of these metallic hydroxides give soluble salts with sodium hydroxide, the addition of excess of sodium hydroxide in such cases causes the disappearance of the original precipitate.

Sodium hydroxide is principally used on the large scale for the manufacture of glass and soaps, and in preparing wood-pulp for the paper industry.

The sodium salts are all derived from the oxide, Na_2O, in which the metal sodium is univalent; they are all soluble in water. The more important ones have already been described, and only a few points remain to be considered.

Sodium chloride (pp. 35, 147) as obtained commercially is often impure, and is sometimes slightly deliquescent owing to the presence of magnesium or calcium chloride.

The pure compound is best prepared by passing hydrogen chloride into a cold (filtered) saturated solution of the commercial substance. Sodium chloride is far less soluble in concentrated hydrochloric acid than in water (a property which is shown by other soluble chlorides, p. 397), and as the gas dissolves, crystals of sodium chloride are precipitated. These crystals are washed by decantation with concentrated hydrochloric acid, drained on an asbestos filter, and finally heated strongly.

Sodium bromide and sodium iodide may be prepared from the bromate and iodate respectively, as previously mentioned (p. 433).

Other important sodium salts are the carbonate (pp. 273, 275), sulphate (p. 226), acetate (p. 279), thiosulphate (p. 496), nitrate (pp. 241, 414), nitrite (p. 527), phosphate (p. 549), and tetraborate (p. 607).

Sodium salts impart an intense yellow colouration to a non-luminous flame.

POTASSIUM, K; AT. WT. 39·1.

The chemical relationship between sodium and potassium is a very close one, and extends to nearly all the compounds of the two elements; so much is this the case that a potassium compound may be used instead of the corresponding sodium compound, and *vice versâ*, in almost any reaction in which either takes part.

Potassium hydroxide, for example, may nearly always be employed instead of sodium hydroxide; although it is rather more active than the latter, the two compounds usually give similar results. For these reasons potassium and its derivatives need only a brief description.

Potassium occurs in nature in forms of combination corresponding with those of sodium, but is far less abundant. The principal source of these compounds is the vast saline deposit which occurs in the neighbourhood of Stassfurth, and which has been produced by the evaporation of sea-water during, it is supposed, a period of some 15,000 years.

This deposit, which covers an area of about 100 square miles, consists of layers of various salts, or double salts, or mixtures which crystallised out one after the other as the solution evaporated. In addition to rock-salt, the principal components of the deposit are carnallite (which forms a layer 50–150 feet in thickness), kainite, sylvine, and kieserite (compare p. 619).

Potassium silicate occurs in small quantities in many igneous rocks (p. 290), associated with other silicates, as, for example, in orthoclase (p. 291); during the weathering of such rocks the potassium silicate is dissolved and passes into the soil, whence it, or other potassium salts formed from it, is absorbed by plants. Potassium compounds are essential to vegetable growth, and the ashes of land-plants were at one time the principal source of potassium carbonate. From vegetable matter taken as food, potassium salts pass into animal organisms, to which also they are essential. Potassium nitrate (p. 241) is an important naturally occurring salt.*

Potassium is manufactured in small quantities only; it is obtained by the electrolysis of fused potassium chloride in much the same way as sodium is obtained from sodium chloride, and also by very strongly heating an intimate mixture of potassium carbonate and carbon,

$$K_2CO_3 + 2C = 2K + 3CO.$$

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* The water in which sheep-wool has been washed contains soluble potassium salts, and when these are ignited they yield potassium carbonate.

The mixture, prepared by heating crude potassium hydrogen tartrate (argol, p. 282), is heated in iron cylinders coated with clay, and the potassium, which volatilises, is condensed in shallow, air-cooled iron boxes. Sodium was formerly prepared from sodium carbonate in a similar manner.

Potassium is plastic, and is easily cut with a knife; it has a silvery lustre, and its sp. gr. is 0·87; it melts at 62·5°. It rapidly tarnishes on exposure to the air, and for this reason it is stored under petroleum. When thrown on water it liberates hydrogen, and the gas immediately takes fire, burning with a flame which is coloured violet or lilac owing to the volatilisation of the metal; a solution of potassium hydroxide is produced,

$$2K + 2H_2O = 2KOH + H_2.*$$

Two oxides of potassium may be formed by heating the metal in dried air which has been freed from carbon dioxide, but neither has been obtained in a pure state. At high temperatures the principal product is a colourless *monoxide*, K_2O, corresponding with the salt-forming oxide, Na_2O; but at low temperatures the principal product is *potassium peroxide*, KO_2, a yellow powder, which acts violently on water, potassium hydroxide, hydrogen peroxide (or water and oxygen), and oxygen being formed.

Potassium hydroxide, KOH (caustic potash, p. 79), is prepared from potassium carbonate, or by the electrolysis of potassium chloride, under conditions similar to those already described in the case of sodium hydroxide (p. 672).

Potassium carbonate, K_2CO_3 (p. 276), may also be obtained from the potassium chloride of the Stassfurth deposit by a method similar to the Leblanc process for the manufacture of sodium carbonate from sodium chloride. It differs from sodium carbonate in being deliquescent.

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* Clean pieces of potassium, about the size of a pea, should be used in this experiment, and the metal should not be handled; as a rule, the experiment is free from danger, but is most safely conducted and viewed from behind a glass screen.

Potassium iodide, KI, and **potassium bromide**, KBr, resemble the chloride (p. 150), and may be prepared by the methods already given (p. 433); they both crystallise in cubes, are readily soluble in water, and are much used in photography and in medicine.

Although nearly all potassium salts are soluble in water, a few of them are so sparingly soluble that they may be obtained by precipitation; of these, potassium hydrogen tartrate and potassium platinichloride are often used in qualitative analysis.

Potassium hydrogen tartrate, $KC_4H_5O_6$ (p. 282), is obtained as a crystalline precipitate when a not too dilute solution of a potassium salt is mixed with a cold, saturated solution of tartaric acid (or of sodium hydrogen tartrate, $NaC_4H_5O_6$, a salt which is readily soluble in water),

$$KCl + C_4H_6O_6 = KC_4H_5O_6 + HCl$$
$$KCl + NaC_4H_5O_6 = KC_4H_5O_6 + NaCl.$$

Unless the solutions are very concentrated the precipitate may not form until the inside surface of the vessel containing the mixture is rubbed (below the level of the liquid) with a glass rod, because potassium hydrogen tartrate is prone to form supersaturated solutions (p. 312).

Potassium platinichloride, K_2PtCl_6, is obtained as a yellow crystalline precipitate when a solution of a potassium salt is added to a solution of 'platinic chloride' (p. 712),

$$2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl$$
$$K_2SO_4 + H_2PtCl_6 = K_2PtCl_6 + H_2SO_4.$$

As in the case of potassium hydrogen tartrate, precipitation may not occur until the solution is disturbed in the above-described manner. Compounds corresponding with these two potassium salts, namely, **ammonium hydrogen tartrate**, $(NH_4)C_4H_5O_6$, and **ammonium platinichloride**, $(NH_4)_2PtCl_6$, are precipitated from solutions of ammonium salts on the addition of tartaric acid or platinic chloride respectively.

This fact should be borne in mind in testing for potassium compounds.

The violet or lilac colouration imparted to a Bunsen-flame when a volatile potassium compound is heated in it also serves for the detection of such compounds.

Other important potassium salts which have been described are the nitrate (p. 241), nitrite (p. 527), chlorate (p. 434), permanganate (p. 450), and dichromate (p. 504).

Potassium cyanide, KCN, is a very important salt which may be obtained by strongly heating *potassium ferrocyanide*,*

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

It is extremely poisonous, and is readily soluble in water; it is used in the laboratory and on the large scale for many different purposes (pp. 662, 663, 708).

Sodium and potassium (and the other alkali metals) differ from other metals in several important respects; their normal carbonates, phosphates, and silicates are soluble in water; their nitrates give nitrites when they are strongly heated, and not metallic oxides; their carbonates and their hydroxides are not decomposed even at very high temperatures.

Rubidium, Rb, and **cæsium,** Cs, are two very rare elements, compounds of which occur in minute quantities in many mineral waters and in some plants. They were the first elements to be discovered with the aid of spectrum analysis (p. 687), and their names refer to the characteristic lines (red and blue respectively) of their spectra.

In chemical properties these two elements are very similar to potassium; in fact, the relationship between these three metals is probably closer even than that between the members of the calcium family. For this reason rubidium and cæsium need not be described; a general idea of their properties will be given by the facts mentioned below.

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* The cyanides are described elsewhere (*Organic Chemistry*, Perkin and Kipping; W. & R. Chambers).

RELATIONSHIP OF THE ALKALI METALS.

The five elements which are classed as the alkali metals show a very close relationship in their general characteristics, and are all univalent. Their corresponding compounds are all very similar in properties, but at the same time show the usual gradation. Of the five elements which comprise this sub-family, lithium and sodium belong to short periods, and in consequence differ in some respects from the other three metals.

These statements summarise the conditions which obtain in this sub-family, and are based on facts such as the following: The five elements, arranged in the order of their increasing atomic weights, show a graded change in physical properties, as illustrated by the data given later (p. 724); the physical properties of corresponding compounds also show a graded change. The elements resemble one another chemically in reacting vigorously with water, in forming strongly basic hydroxides, and in the various other important respects, mentioned under sodium and potassium (p. 679), in which they differ from other metals.

Family I. of the periodic system includes the alkali metals and the copper sub-family, and it might perhaps be expected that the relation between these two sub-families would be of the same nature as between the two sub-families of Family II. This, however, is not the case. The position of copper, silver, and gold (between the members of Family VIII. and those of the magnesium sub-family, see sheet facing the end of the index) precludes any close resemblance between them and the alkali metals, just as the position of manganese precludes the exhibition of analogy with the halogens.

The only respect in which the two branches of Family I. resemble one another is in the formation of compounds in which the elements are univalent; but even between corresponding compounds of similar type there is practically no analogy except that they are often isomorphous.

CHAPTER LXI.

The Helium or Argon Family.

In comparatively recent times two great advances have been made in the science of chemistry. One of these is the discovery of argon and the other members of the argon family, the other the discovery of radium and the phenomena of radio-activity (p. 729).

The history of the discovery of argon is full of interest. Even so long ago as 1784 certain observations of Cavendish seemed to show that the atmosphere might contain unrecognised gases; these observations, however, were not followed up by him; they completely failed to attract attention, and were in fact forgotten. About 1892 it was proved by Rayleigh that the density of gaseous nitrogen obtained from the atmosphere was very slightly greater than that of nitrogen prepared from ammonia, nitric oxide, or other nitrogen compounds. Thus a litre of most carefully purified atmospheric nitrogen weighed 1·2572 g. at N.T.P., whereas the same volume of purified gas prepared from a nitrogen compound weighed only 1·2521 g. Small though this difference was, it could not be attributed to experimental error or to the presence of any known substance as impurity. Consequently it was concluded that atmospheric nitrogen contained some gas having a density greater than that of nitrogen. This conclusion led to further investigations by Rayleigh and Ramsay, and thus to the discovery of the element **argon**.

Many processes have already been described (pp. 88–92) by means of which oxygen may be abstracted from the atmosphere; it has also been shown that nitrogen is absorbed by strongly heated magnesium (p. 517). One of the methods by which argon and the other inert gases were first obtained from the atmosphere consisted in removing the oxygen, by passing the air over heated copper, and then absorbing the nitrogen with strongly heated magnesium. Another method was to 'spark' air with oxygen in presence of potassium hydroxide solution until (most or) the whole of the nitrogen had been converted into the tetroxide (p. 247) or dioxide (p. 350),* and then to absorb the remaining oxygen (and nitrogen) by the processes just mentioned.

In either case there remains a very small proportion (about 1 per cent., p. 95) of the original volume of air, and this residue is not chemically changed by any known substance; to this residual, colourless gas the name *argon* was given.

Further investigation by Ramsay showed that this residue contained about 1 per cent. of a mixture of four other gases; one of these proved to be identical with an element, **helium**, which, with the aid of spectrum analysis (p. 685), had been detected by Frankland and Lockyer (in 1868) in the sun's atmosphere, and which therefore had been discovered by them some thirty years before its existence in the earth's atmosphere was proved; † the others were named **neon** (Ne), **krypton** (Kr), and **xenon** (X), respectively.

As all these gases are absolutely inert, and so far as is known are incapable of forming any compounds, their separation had to be accomplished entirely by physical methods; for this purpose fractional distillation (p. 32) was employed.

When any ordinary gas (as distinguished from a perfect gas, footnote, p. 163) is allowed to expand, its temperature is usually lowered to some extent because of the work done in overcoming the cohesion of its molecules. Further, if a compressed gas is allowed to escape continuously from a small aperture into the air, the gas is continuously cooled, because of the work done against the atmospheric pressure; thus on the tap of a cylinder which contains highly compressed carbon dioxide being opened widely the cooling effect is so great that some of the gas is frozen to a colourless crystalline solid, which may be collected in a cloth loosely wrapped round the tap.

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* As the concentration of the nitrogen tetroxide remains inappreciable owing to the immediate absorption of the gas by the alkaline solution, the reversible reactions previously described (p. 299) proceed in the direction giving the oxide until practically the whole of the nitrogen is removed.

† Helium was first obtained by Ramsay from certain rare minerals such as cleveite and uranite, in which it is produced by the disintegration of radio-active elements (p. 733). It also occurs in extremely minute quantities in certain mineral waters. Helium is the only gas which has not yet been solidified.

Now, if a metal tube (*a*, fig. 116) containing a highly compressed gas is surrounded by a larger tube (*b*), and the expanded and cooled gas escaping from the outlet (*c*) is caused to pass back again around the narrower tube (*a*), the compressed gas in the latter is cooled *before* it expands, and when it expands its temperature is further lowered. By continuing the process, the temperature of the gas at the moment of its expansion may be reduced to such an extent that part of the gas liquefies as it escapes from the nozzle (*c*), and collects in the chamber (*d*).

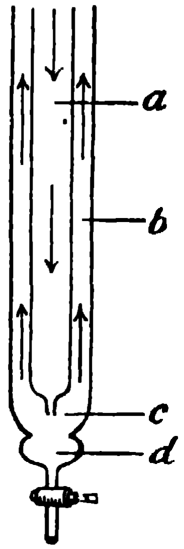

Fig. 116.

This is the principle of the process now used for obtaining liquid 'air' with the aid of apparatus devised by Linde and by Hampson. In these 'machines,' instead of the straight tubes shown above, the two streams of air are brought into much more intimate contact in spirally arranged tubes many feet in length. The compressed air escapes under a pressure of 150–200 atmospheres, while the pressure of the expanded gas is maintained at one atmosphere.

Vessels in which liquid air and other liquids of very low boiling-point may be kept for a considerable time under atmospheric pressure were devised by Dewar, who in comparatively recent times has succeeded in liquefying hydrogen in large quantities.* They consist of double-walled glass bulbs (fig. 117), the space between the walls being completely exhausted so that heat cannot be conducted from the outside air to the liquid; in some bulbs the surfaces of the vessels are silvered in order that they may reflect radiant heat.

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* For measuring the low temperatures reached in such experiments ordinary thermometers are of course useless, and a platinum *resistance thermometer* is employed. The resistance offered by platinum to the passage of an electric current varies regularly with the temperature of the metal.

For the isolation of the inert gases of the atmosphere fractional distillation may be applied either to liquid 'air' or to the crude 'argon' which is obtained from the atmosphere by the methods just described.

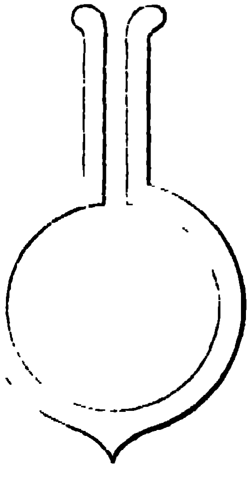

Fig. 117.

Liquid 'air' varies in composition. Since nitrogen (b.p. - 194°) is more volatile than oxygen (b.p. - 182·5°), the liquid 'air' contains a larger proportion (about 55 per cent.) of oxygen, while the gas which escapes liquefaction contains a larger proportion of nitrogen (and of helium and neon), than does the atmosphere. This less easily condensed portion may first be freed from nitrogen by chemical methods and then cooled with liquid hydrogen; neon (b.p. - 233°) is thus liquefied, while helium (b.p. - 267° ?) remains in a gaseous state and may be pumped off. The more easily condensed portion, or liquid 'air,' when allowed to evaporate slowly in a Dewar flask, first loses almost pure nitrogen. After some time the residue consists almost entirely of oxygen (and in this way oxygen may be prepared from the atmosphere for commercial purposes); but when this liquid is slowly evaporated, it finally affords, in order, argon (b.p. - 186°), krypton (b.p. - 152°), and xenon (b.p. - 109°). Each of these products is purified by repeated fractional distillation.

In the case of crude argon, this may be liquefied by cooling it with liquid 'air,' and then fractionally distilled; the dissolved helium and neon escape first, while the krypton and xenon remain in the last fractions.

The five gases named above seem to be incapable of undergoing chemical change no matter under what conditions they are placed. Obviously in these circumstances their *atomic* weights cannot be determined by the method previously described, which is to find the smallest quantity of the element which is contained in the gram-molecule of any of its compounds (pp. 195–198). The *molecular* weights of the elements may, of course, be obtained directly from their densities in the usual manner; but in order to ascertain their atomic weights it is further necessary to know the number of atoms in their molecules.

Now the molecular heat of a gas under *constant volume* is the amount of heat required to raise the temperature of 22·4 litres of the gas (measured at N.T.P.) through 1°. In the case of a perfect gas (footnote, p. 163) this value can be calculated, and is found to be 3 calories; but with most gases more than 3 calories are required, because of the heat absorbed in doing work within the molecules of the gas. The heat expended in doing this work depends on the molecular complexity of the gas; in monatomic gases (p. 383) it is nil—that is to say, the molecular heat of a monatomic vapour such as mercury (p. 630) is 3 calories; in diatomic gases the molecular heat is about 5, in triatomic gases about 7·5, calories, and so on. Consequently, if the molecular heat of a gas can be determined the *atomicity* of the molecule (the number of atoms in the molecule) is known.

As it has been found that the molecular heat of argon and of the other gases of this family is approximately 3 calories,* it follows that these gases are monatomic; consequently their atomic weights are identical with their molecular weights.

SPECTRUM ANALYSIS.

The inert gases described above, as will be obvious from their properties, cannot be distinguished or identified by chemical tests, and yet it is possible to recognise with certainty a quantity of any one of them which is far too small to be measured; this is accomplished with the aid of *spectrum analysis*.

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* The molecular heat was determined from a measurement of the velocity of sound in the gas—that is to say, by Kundt's method (described in text-books on physics) of determining the ratio $\frac{C_p}{C_v}$ of a gas.

When white light from an incandescent solid such as platinum, or quicklime (p. 134), or carbon (p. 133), is passed through a prism and undergoes *dispersion*, there results a *continuous spectrum*; that is to say, light of all wave-lengths between those of the visible violet and the visible red rays is seen in the spectrum (Plate I.). When, however, the light from a glowing gas or vapour is examined in this way the resulting spectrum is *discontinuous*, and consists either of a number of lines (*line-spectrum*) or of a number of bands (*band-spectrum*) according to the nature and temperature of the incandescent substance. If, for example, a little sodium chloride is introduced into the (non-luminous) Bunsen-flame, and the light from the flame is examined with a *spectroscope*, there is no continuous spectrum to be seen, but only a single bright-yellow line (Plate I.), which occupies the same position in the spectrum as would the yellow light of this particular wave-length, had the spectrum been that of an incandescent solid; this yellow line is given by all *sodium* compounds.* Similarly, when potassium chloride is introduced into a Bunsen-flame and the light is examined with a spectroscope, the spectrum is seen to consist of two lines, one bright red and the other blue (Plate I.), which occupy respectively the same positions as light of the same wave-lengths in a continuous spectrum; these two lines are given by all potassium compounds.*

Now, every element gives a *characteristic* spectrum by means of which it can be identified; moreover, the quantity of any element required to give a spectrum is extremely small. Hence the spectroscope affords a means of identifying with absolute certainty quantities of matter which are so minute that they are not weighable even on the most delicate balance; in the case of some elements it is thus possible to identify 10^{-6} to 10^{-9} gram.

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* The spectrum of the *gas* chlorine is so faint that it is barely visible under these conditions. With extremely delicate spectroscopes, in the place of the single sodium line, two lines are seen very close together.

Spectrum analysis was first brought into use in 1859 by Bunsen and Kirchhoff, and almost immediately afterwards (in 1860) the great value of this new method was strikingly demonstrated by the discovery with its aid of the two elements, rubidium and cæsium (Plate I.); since that time many other elements have been discovered with the aid of the spectroscope.

The spectrum of a *compound* shows the lines of the *elements* of which it is composed provided that the compound is sufficiently heated, and is thus decomposed into its constituent elements; similarly, a mixture of elements or of compounds shows the characteristic lines of each of the elements present. If, for example, a mixture of, say, sodium and potassium chlorides is heated in a Bunsen-flame, the intense yellow colouration produced by the sodium may completely mask the violet colouration given by the potassium when the flame is examined with the naked eye; when, however, the spectroscope is employed the characteristic lines of both metals are distinctly observed.

Instead of some of the substance being simply heated on the end of a platinum wire in a Bunsen-flame, electric sparks may be passed between two platinum wires the ends of which have been dipped into the substance, or between two carbon rods which have been impregnated with the substance; in the case of metals, sparks may be passed between two wires of the metal.

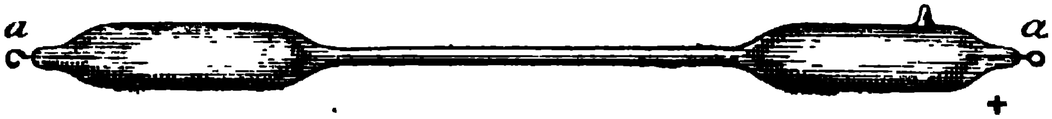

Fig. 118.

The spectra of *gases* are obtained with the aid of Geissler or Plücker tubes (fig. 118). The tube is provided with platinum terminals (*a*, *a*) and contains the gas under a very low pressure. On the terminals (*a*, *a*) being connected with those of an induction coil, and a discharge being passed, the whole tube glows, and the emitted light (best that from the very narrow middle portion of the tube) may be examined with the spectroscope.

It was in this way that the inert gases of the atmosphere were proved to be new substances, and their spectra being now known, they may be detected and identified with absolute certainty by spectrum analysis.

When light from an incandescent solid is passed through a transparent solid, liquid, or solution, some of the light-waves are absorbed; the *transmitted* light does not give a continuous spectrum, but one which is broken by dark spaces, and the positions and breadths of these dark spaces depend on (*a*) the nature of the substance examined, (*b*) the thickness of the layer through which the light has passed. Spectra thus obtained are called *absorption spectra;* they are often highly characteristic, and may then serve for purposes of identification.

The light from the sun, when examined with a delicate spectroscope, gives a spectrum in which appear a very large number of dark lines; these were first noticed by Fraunhofer, and are known as Fraunhofer's lines. A great many of these *dark* lines occupy positions in the spectrum which correspond with those of the *bright* lines given by some of the common elements (Plate I.). This fact is explained as follows: When white light is passed through a vapour or a gas which is at a lower temperature than the incandescent source of light, this vapour or gas absorbs those waves which it itself gives out when it is incandescent. The sun is an incandescent mass surrounded by gases and vapours which, being at a lower temperature than the sun, absorb certain waves; as many of the waves which are thus absorbed are identical with those given out by incandescent terrestrial elements, it must be concluded that many of these elements are contained in the sun.

Spectrum analysis, therefore, renders it possible to identify the constituents of heavenly bodies; by this means it has been found, not only that many (more than thirty-four) of the terrestrial elements are contained in the sun, but that many of them are also present in the stars.

CHAPTER LXII.

Iron, Nickel, Cobalt, and Related Metals.

Iron, nickel, and cobalt do not form a natural family comparable to those already studied, and their relationship to one another and to the other metals described in this chapter may be left for later consideration (p. 709). It will be sufficient to point out here that although iron, nickel, and cobalt all form very similar compounds, in which the elements are bivalent, these compounds cannot be regarded as typical, and in some respects iron is more closely related to manganese and even to chromium than to nickel and cobalt. One noteworthy resemblance between iron, nickel, and cobalt is that they are all attracted by a magnet.

IRON, Fe; AT. WT. 55·8.

Iron, the most important of all metals, is rarely found in a free state except in the form of *meteoric iron*, which, in small particles constantly and in large masses occasionally, reaches the earth from the world beyond.*

The principal compounds from which the metal is extracted are the oxides, Fe_2O_3 and Fe_3O_4, and the carbonate, $FeCO_3$, which occur in vast quantities in many parts of the world, often in close proximity to the coal-measures.

Of the more important ores, the following may be mentioned:* *red hæmatite* (a brown earthy mass), *specular iron ore* (a gray crystalline mineral), and *kidney ore* (brownish-red nodules), which are varieties of ferric oxide, Fe_2O_3; *brown hæmatite* (a dark reddish-brown mineral), *yellow ochre*, and *bog iron ore*, which consist of a hydrated ferric oxide, $Fe_2O_3, 2Fe(OH)_3$; *magnetite*, *magnetic iron ore*, or *lodestone*, a black, often crystalline mineral of a high degree of purity, consisting of Fe_3O_4; *siderite* or *spathic iron ore*, a yellowish-brown crystalline mineral (when mixed with clay it is known as *clay ironstone*, and when in addition it contains coal it is known as *blackband ironstone*). These spathic ores all contain ferrous carbonate, $FeCO_3$, mixed with variable quantities of the carbonates of manganese, calcium, and magnesium.

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* Some masses of meteoric iron weigh as much as twenty tons. Meteorites always contain nickel in considerable quantities; cobalt, copper, carbon, and many other elements are also often present in small quantities.

Small quantities of combined iron are contained in all plants and animals, to the life of which iron is essential; chlorophyll (p. 139), for example, and hæmoglobin (the coloured matter of the blood), contain iron compounds. Many natural waters contain a little ferrous carbonate in solution (chalybeate waters); such waters give a red deposit of hydrated ferric oxide on exposure to the air.

The Manufacture of Cast-Iron or Pig-Iron.—Ferrous carbonate is converted into ferrous oxide at relatively low temperatures. This compound and the higher oxides of iron are easily reduced to the metal when they are heated in a stream of carbon monoxide (p. 288). These reactions are made use of in the extraction of iron from its ores; but many other changes occur during this operation, and the crude product is highly impure. The reason of this is that the ores contain earthy matter (silica, clay, limestone, &c.), and in order to separate the metal, after it has been formed by the reduction of its oxides, it is necessary to melt not only the iron, but also the whole of the earthy matter with which the metal is mixed. For this purpose a *flux* (p. 585) must usually be added, and even then a very high temperature is required. At this high temperature the molten iron dissolves or combines with *carbon* from the fuel, and with *silicon*, *phosphorus*, and *sulphur* which are formed by the reduction of the silicates, phosphates, and sulphates present in the ores. These elements, together with more or less *manganese* (formed by the reduction of manganese compounds, which are nearly always present), are all contained in the crude iron (pig-iron), and together form some 6–10 per cent. of the product.

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* Iron pyrites (p. 221), although abundant, is not usually classed as an iron ore, and is chiefly employed as a source of sulphur dioxide; the ferric oxide which remains when pyrites is roasted cannot be used for the manufacture of iron by the ordinary methods, owing to the combined sulphur which it retains.

The *smelting* of iron ores is carried out in a *blast-furnace* (fig. 119). This furnace, which is often about 80 feet in height and about 20 feet in greatest internal diameter, is constructed of firebrick, strengthened by sheet-iron or steel. It is completely filled with the furnace charge, a mixture of iron ore, coke (or coal), and flux in suitable proportions; and when once started it is worked continuously, perhaps during several years. The materials are introduced at the top, and by means of the counterpoised cover (*a*) the furnace is kept closed, so that the furnace gas which escapes through the pipe (*b*) may be collected and utilised. Near the hearth or bottom of the furnace a number of blowpipes or twyers, concentrically arranged, pass from the annular pipe (*c*) through the walls, and supply a powerful blast of heated air for the combustion of the fuel. At the very high temperature which is reached here the iron is completely melted, as is also the earthy matter, assisted by the flux. The molten iron collects at the bottom of the furnace, and by removing a clay plug it is run off from time to time into channels formed in sand. The melted slag collects at the surface of the molten iron in the furnace, and flows away continuously through an opening (not shown in the fig.) some distance above the bottom of the hearth.

The principal chemical changes which occur in the process are as follows: Near the bottom of the furnace the coke in the charge burns to carbon dioxide in the heated air-blast, but this gas is soon reduced to carbon monoxide as it rises

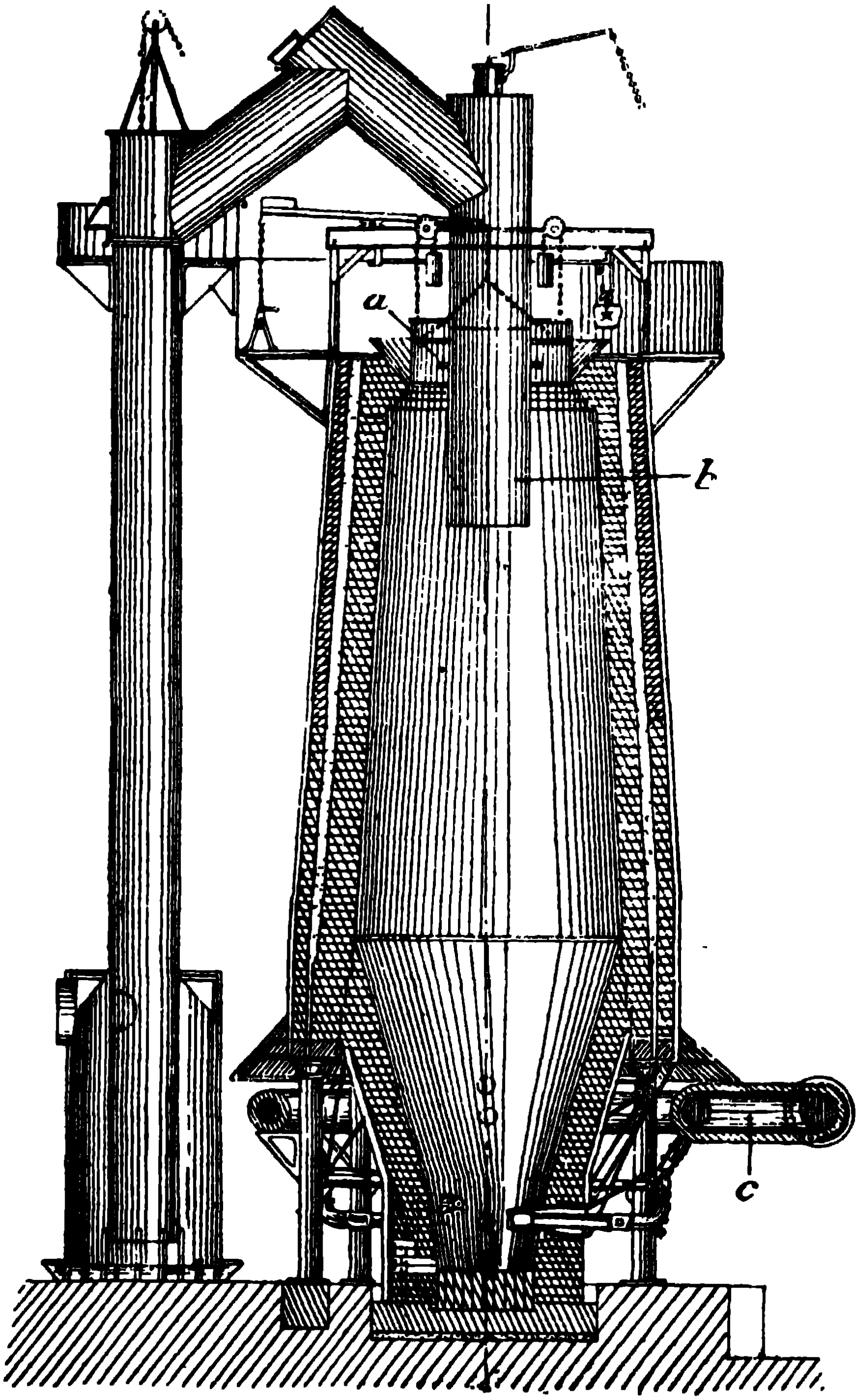

Fig. 119.

through the red-hot coke. High up in the furnace, where the temperature is very much lower, the oxides of iron are reduced by the carbon monoxide (p. 288), and farther down the oxides of manganese likewise undergo reduction. The mixture of finely divided iron, earthy matter, fuel, and flux slowly falls until it reaches the region of high temperature near the twyers; here, as already mentioned, the iron melts and takes up carbon, silicon, phosphorus, sulphur, and manganese, while the earthy matter and the flux react to form a fusible slag.

The products of the blast-furnace are crude *iron* (cast-iron or pig-iron), *slag*, and *furnace gas*.

Cast-iron or pig-iron varies considerably in composition and in properties. Some varieties (*white* cast-iron) show a very light-gray, fine-grained structure, and look homogeneous; others (*gray* cast-iron) show a much darker, coarse-grained structure, and look heterogeneous and distinctly crystalline in parts. Intermediate varieties (*mottled* cast-iron) are also obtained, and in fact the different qualities grade into one another almost insensibly. The difference in properties depends essentially on the form in which the carbon is present in the iron. In white cast-iron most of the carbon is *combined* with the metal, forming iron carbide, whereas in gray cast-iron most of the carbon is present as *free* graphite; in mottled cast-iron the carbon is partly combined and partly free. *Spiegeleisen* is a lustrous crystalline cast-iron which contains 5–20 per cent. of manganese and also a large proportion of carbon. *Ferromanganese* contains about 30 per cent. of manganese and 5–7·5 per cent. of carbon.

The composition of typical samples of white, mottled, and gray cast-iron is indicated below:

	White.	Mottled.	Gray.
Combined carbon . .	2·17	1·66	0·94
Free carbon	0·50	1·56	2·68
Silicon..	0·28	0·52	0·94
Manganese	0·23	1·53	1·21
Phosphorus	1·37	0·63	0·65
Sulphur	0·01	0·03	0·01

White iron is obtained when the crude metal is rapidly cooled; it melts at about 1200° to a pasty mass, which contracts as it solidifies, and, consequently, is not suitable for making castings. When treated with diluted nitric acid it leaves very little residue of (free) carbon, because the combined carbon—that is to say, the iron carbide—is attacked by the acid, giving iron nitrate, and soluble carbon compounds which colour the solution dark brown.

Gray iron is obtained when the crude metal is slowly cooled; it melts at about 1150°, giving a fluid mass which expands as it solidifies, and, consequently, is suitable for making castings. When treated with diluted nitric acid it gives a considerable residue of (free) carbon or graphite, and the solution is only slightly coloured by compounds formed from the small quantity of combined carbon which was present.

The *slag* from a blast-furnace consists essentially of a *mixture* of silicates of aluminium and calcium, but may also contain manganese silicate and a little ferrous silicate. The flux used to produce this slag depends on the nature of the earthy matter in the ore. Thus, when the ores contain sand only, limestone and clay must be added in order to get a *mixture* of calcium and aluminium silicates, which melts at a lower temperature than that at which either of its components, or sand alone, would liquefy.

Slags are utilised in road-making and as ballast on railroads, or they are granulated by running them (while melted) into water, and then mixed with lime and made into 'bricks' or into building cements. Slag-wool, a fibrous, asbestos-like material, is made by blowing a powerful jet of steam on a stream of the molten slag. It is used as a packing for steam-pipes, &c.

Furnace gas consists principally of a mixture of nitrogen (about 57), carbon monoxide (about 27), and carbon dioxide (about 16 per cent. by volume) and is combustible. It is utilised in heating the air-blast, in raising steam, and in working gas-engines. It is not possible to utilise the whole of the carbon monoxide in the furnace for the reduction of the oxides of iron, as the reaction,

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2,$$

is reversible, and therefore a condition of equilibrium it attained. The object of heating the air supplied to the twyers is to lessen the consumption of fuel in the furnace and to obtain a higher temperatute. The air is heated by passing it through chambers

(*Cowper* or *Whitwell stoves*) containing brickwork, which is heated with the aid of the furnace gas.

One large furnace will produce about 200 tons of pig-iron per day. The quantity made in Great Britain alone in 1907 amounted to more than 10 million tons.

Malleable iron.—Cast-iron, the product of the blast-furnace, although very hard, is extremely brittle, and cannot be used directly for engineering purposes except for making castings which do not need to be very strong; for all other purposes the cast-iron must be purified.

Now the physical properties of the products prepared from cast-iron depend to an extraordinary extent on the nature and proportion of the 'impurities' which are left in the iron.

If these impurities are almost entirely eliminated there results a product which contains, say, 99·5 per cent. of iron and less than about 0·3 per cent. of carbon, and which is known as *malleable-* or *wrought-iron*; if, however, a larger proportion, say 0·5–1·5 per cent., of carbon is purposely left in the material, the product is then known as *steel*. These two varieties of 'iron' pass into one another by insensible gradations according to the amount of carbon present; but between extreme varieties there is a vast difference in properties, as will be described later.

For the preparation of malleable iron, the least impure variety of the metal which is manufactured, it is necessary to get rid of the impurities as far as is possible. For this purpose cast-iron, usually the white variety, is melted in a furnace and the impurities are oxidised. Oxidation is accomplished with atmospheric oxygen, and also by lining the furnace-bed with a layer of oxide of iron, or by adding oxide of iron to the molten pig-iron. In either case the oxide of iron is reduced and the carbon in the pig-iron is oxidised to carbon monoxide, while some of the silicon and phosphorus are also oxidised to silica and phosphorus pentoxide respectively, which combine with ferrous oxide to form a fusible slag.

In the *puddling process* the pig-iron is melted in a reverberatory furnace (p. 587), and is constantly stirred by hand or by machinery. The escape of the carbonic oxide causes the appearance of boiling; hence the process is often called *pig-boiling*. As the carbon and other impurities are removed the melting-point of the product rises, and ultimately the malleable iron becomes stiff enough to be formed into balls or *blooms*. These are pressed under a steam hammer to free them from slag, and are then cut and rolled into bars. The bars are reheated, welded together, and again cut and rolled. As a result of these operations, repeated several times, the bars acquire a fibrous structure, and the material is then known as *wrought-iron*.

In the Siemens-Martin process the pig-iron is heated with iron ores and scrap-iron in furnaces fed by gaseous fuel; when the pig-iron is rich in phosphorus the hearth is lined with dolomite, because the basic oxides contained in this material combine with the phosphorus pentoxide. Unless such a lining is used, pig-iron which contains much phosphorus cannot be employed for the preparation of malleable iron, as this impurity is not eliminated in the ordinary puddling process.

The quantity of impurity in two samples of malleable- or wrought-iron is indicated by the following figures:

$C = 0{\cdot}14$, $Si = 0{\cdot}04$, $P = 0{\cdot}07$, $Mn = 0{\cdot}37$, $S = 0{\cdot}08$ per cent.
$C = 0{\cdot}15$, $Si = 0{\cdot}14$, $P = 0{\cdot}21$, $Mn = 0{\cdot}14$, $S = 0{\cdot}04$ per cent.

Steel.—For the manufacture of steel various methods are used. In some of these practically the whole of the carbon and other impurities are removed from pig-iron, and to the malleable iron thus obtained iron rich in carbon is then added, in quantities sufficient to convert the whole into steel.

The *Bessemer process* is based primarily on the fact that when air is blown through a mass of molten pig-iron the heat generated by the oxidation of the silicon, manganese, carbon, and some of the iron, is sufficient to keep the whole mass liquid until the impurities are eliminated.

The operation is carried out in a large *converter* (fig. 120), which takes a charge of 15–18 tons. The converter is made of sheet-iron, heavily lined on the inside with a fire-resisting layer of a siliceous earth (ganister). From the pipe (*a*), air at high pressure (18–20 lbs. per sq. in.) can be forced into the chamber (*b*), from which it passes through a number of channels (*c*, *c*) in the lining of the bottom of the converter. The converter is mounted on trunnions, and by means of suitable machinery, it may be rotated about its horizontal axis through an angle of about 180°.

The converter, having been thoroughly heated, is placed in a nearly horizontal position, and the charge of cast-iron, previously melted in a small furnace, is run in. The converter is then rotated until it is vertical, and at the same time the air-blast is started. At first the silicon and manganese and a little iron begin to oxidise, but after some four minutes the carbon begins to burn, and a flame of carbonic oxide soon appears at the mouth of the converter, the oxide of iron which has been formed undergoing reduction; after the lapse of a further fourteen to sixteen minutes the flame suddenly dies down, and the converter then contains *malleable iron*.

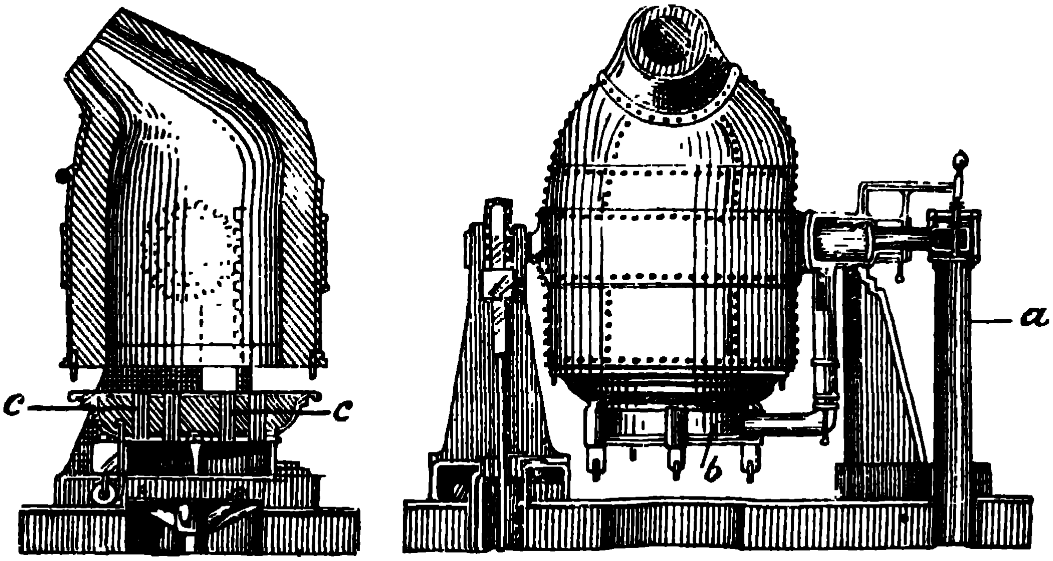

Fig. 120.

In order to transform this product into steel, the converter is again turned on its side and a suitable proportion (say 10 per cent.) of spiegeleisen or ferromanganese (rich in carbon, p. 693) is added; the contents of the converter are then mixed by starting the air-blast for a moment, and the *steel* thus formed is cast into moulds.

When the Bessemer process was first invented (in 1856), pig-iron containing phosphorus could not be used for the manufacture of Bessemer steel, as this impurity was not removed. This great difficulty was overcome (in 1880) by Thomas and Gilchrist, who employed a *basic lining* (dolomite) for the converter, instead of the *acid lining* (ganister) which had been used up to that time, and also added some lime to the contents of the converter. Phosphorus pentoxide unites with the basic oxides of calcium and magnesium in the dolomite, and with this lining it is actually advantageous to employ pig-iron which is rich in phosphorus, as the whole of the phosphorus is obtained in the form of a phosphate (Thomas slag, basic slag) which is valuable as a manure.

The following analyses show (I.) the composition of the pig-iron, (II.) that of the converter contents before the addition of the spiegeleisen, (III.) that of the spiegeleisen, and (IV.) that of the finished Bessemer steel (an acid lining being used):

	C	Si	S	P	Mn
I. . . .	3·10	0·98	0·06	0·10	0·40
II. . . .	0·04	0·02	0·06	0·10	0·01
III. . . .	4·64	0·05	—	0·14	14·90
IV. . . .	0·45	0·04	0·06	0·10	1·15

The *cementation* process for the manufacture of steel depends on the fact that when bars of wrought-iron (p. 696) are embedded in powdered charcoal in air-tight chambers which are strongly heated, the iron becomes impregnated with carbon, and in the course of some seven to ten days is converted into steel. This product, called ***blister-steel***, on account of the 'blisters' which form at the surface of the bars, is melted in graphite crucibles and then cast into moulds. Though the cementation process is a very slow one in comparison with the Bessemer process, it affords steel of high quality, which is used principally for the manufacture of tools and cutlery.

Malleable iron may be transformed superficially into steel by heating it for a short time in powdered charcoal; this process is used for small tools, &c., and is termed *case-hardening*.

The *open-hearth* process for the manufacture of steel is much the same as the Siemens-Martin process for the manufacture of malleable iron; the product is tested from time to time, and the operation is stopped when sufficient carbon to give steel still remains in the iron. The material thus produced is very similar to malleable iron, and generally contains less than 0·5 per cent. of carbon.

THE PROPERTIES OF MALLEABLE IRON AND STEEL.

The essential difference in composition between malleable iron and steel is that the latter contains the more carbon; in malleable iron the quantity of carbon is generally below, say, 0·3 per cent., while in steel it is generally above, say, 0·4 per cent., and may reach as much as 1·0 or more. Hence samples of iron containing from about 0·3 to about 0·4 per cent. of carbon may be classed as malleable iron, or as *mild, low-carbon*, or *malleable steel.*

Malleable iron, as its name implies, may be rolled or hammered when it is hot, and may be drawn into wire; it may also be welded— that is to say, two red-hot pieces may be worked together to form a homogeneous whole. Malleable iron is relatively soft and non-elastic, but is tough. It is easily magnetised, but it soon loses its magnetism again. Sulphur or phosphorus make malleable iron brittle when hot (*red-short*) or when cold (*cold-short*) respectively.

The properties of malleable iron do not undergo any change when the metal is made red-hot and then suddenly or slowly cooled.

Steel is much harder than malleable iron, and except in the case of low-carbon steels cannot be worked so easily as malleable iron, nor can it be welded. Its tenacity or *tensile strength* is much greater than that of malleable iron. It is not easily magnetised, but it does not lose its magnetism again readily. Sulphur and phosphorus affect it as they do malleable iron.

The properties of steel are completely changed when the metal is heated above 770° and then suddenly cooled by plunging it into water; it becomes very much harder, and much more brittle. This process of treating steel is known as *hardening*. Steel which has been hardened, if heated to

220–300° and then allowed to cool, becomes softer and tougher, and the extent to which the hardened steel is changed depends on the temperature to which it is heated; this process of treating hardened steel is known as *tempering*.

By combining these processes, steel of almost any desired hardness, elasticity, &c., can be obtained, and thus a given material may be rendered suitable for a great variety of very different purposes.

These changes may be shown by heating a portion of a watch-spring (tempered steel) to a red-heat in a Bunsen-burner, and then suddenly plunging it into cold water or mercury; the steel is then so brittle that it is easily broken into small pieces between the thumb and fingers, and so hard that it will scratch glass. If now this hardened steel is heated in a metal-bath at about 260° and then allowed to cool, it becomes tough and much softer. A piece of malleable- or wrought-iron wire treated in a similar manner remains unchanged.

A great many varieties of steel, containing nickel, manganese, chromium, or other elements, are now manufactured; each of these has certain properties which render it especially suitable for some particular purpose.

Some, or the whole, of the carbon contained in steel is present in a combined form, probably as *carbide of iron*, Fe_3C. Various views have been advanced to account for the great variation in properties of different qualities of steel and of identical qualities of steel which have been differently treated.

Pure iron is capable of existing in three allotropic forms which are converted one into the other at certain temperatures. These modifications differ in crystalline form and in other physical properties (hardness, tenacity, elasticity, &c.), and also in the readiness with which they dissolve carbide of iron.

α-Ferrite, which exists below about 770°, is soft and magnetic, and only a very poor solvent for carbide of iron. *β-Ferrite*, which exists from about 770 to 890°, is hard and non-magnetic. *γ-Ferrite*, which exists from above 890°, is also non-magnetic.

According to one explanation of the behaviour of steel, the unhardened metal, which consists of α-ferrite, changes at about 770° into the β-form; if now this is suddenly cooled, it does not pass back again into the soft α-form, owing to the presence of the carbide of iron, but if very little of the latter is present the soft α-form is reproduced.

Another explanation of the behaviour of steel is as follows: The maximum quantity of carbon which can be taken up by pure molten iron is 4·8 per cent.; on cooling, some of the carbon separates as graphite until a eutectic (p. 315), containing 4·3 per cent. of carbon and melting at 1130°, is formed. After this eutectic has solidified a further quantity of graphite separates, leaving an alloy or solid solution of iron and iron carbide, containing 2 per cent. of carbon, and known as *martensite.* On this alloy cooling to about 1000°, the martensite begins to change into a heterogeneous mixture of *cementite* (6·7 per cent. of carbon) or carbide of iron, Fe_3C, and an alloy or solid solution of iron and cementite, which contains only 0·85 per cent. of carbon, but which is still known as martensite (or sorbite). From about 690° the rest of the martensite (or sorbite) begins to change into cementite, and the material finally consists of a soft, heterogeneous mass of cementite and pure iron (ferrite). When the steel is suddenly cooled, the martensite, which forms the red-hot material, does not pass into cementite and ferrite, but remains in a metastable condition (p. 313); by reheating to about 220–300° some of the martensite undergoes change and the steel is tempered.

PURE IRON AND ITS PROPERTIES.

Pure iron is seldom met with, but may be obtained by reducing pure ferric oxide with pure hydrogen at about 600°.*

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* When reduction takes place at a low temperature the product is pyrophoric; that is to say, it glows on exposure to the air (especially if warm), and is converted into oxide.

Ferrum redactum is a variable mixture of iron and iron oxide used in pharmacy.

In the massive state it is silvery-white and soft; has a sp. gr. 7·78, and melts at about 1600°.

Iron is not appreciably attacked by dry air or by pure water, but it rapidly rusts under ordinary conditions; this appears to be due to the action of carbonic acid, which attacks iron readily,

$$Fe + H_2CO_3 = FeCO_3 + H_2.$$

The *ferrous carbonate* thus formed is very unstable, and in aqueous solution it undergoes hydrolysis and oxidation, giving ferric hydroxide. The rusting of iron is prevented by coating the metal with tin (p. 588), zinc (p. 625), or nickel (p. 706); also by painting or varnishing it.

Iron which has been dipped in nitric acid of sp. gr. 1·4, or in certain other solutions, and then washed with water, is not attacked by nitric acid, and is said to be *passive*: a similar behaviour is shown by certain other metals, but a satisfactory explanation of these facts is still wanting.

Iron forms two basic oxides, *ferrous oxide*, FeO, and *ferric oxide*, Fe_2O_3, from each of which a series of corresponding salts is obtained. The *black oxide*, Fe_3O_4, which occurs in nature, and which is formed when iron is heated in the air (smithy scale), or in steam, is not a basic oxide; when treated with acids it gives a mixture of a ferrous and a ferric salt, and thus behaves as if it were a compound of FeO and Fe_2O_3.

FERROUS COMPOUNDS.

Most of the ferrous salts may be directly obtained by treating iron with the required acid; but, owing to the readiness with which these salts undergo oxidation, care must be taken to exclude atmospheric oxygen, especially when the evolution of hydrogen has ceased. So long as hydrogen is being generated, any ferric salt which is formed is reduced again to the ferrous compound. Anhydrous ferrous salts are generally colourless, yellow, or brown, but the hydrated salts are usually green.

Ferrous hydroxide, $Fe(OH)_2$, is obtained as a pale-green flocculent precipitate on sodium hydroxide being added to a solution of a ferrous salt. It is slightly soluble in water, giving an alkaline solution, and it rapidly absorbs oxygen, giving ferric hydroxide. **Ferrous oxide**, FeO, a black solid, is most conveniently obtained by igniting *ferrous oxalate*, FeC_2O_4, out of contact with the air.

Ferrous chloride, $FeCl_2, 4H_2O$, is a green crystalline substance; the anhydrous salt is colourless, and may be obtained by heating iron in a stream of dry hydrogen chloride.

Ferrous sulphate, $FeSO_4, 7H_2O$ (pp. 37, 226), is the commonest ferrous salt. It oxidises on exposure to the air; but the pale-green double salt (p. 322) which it forms with ammonium sulphate—**ferrous ammonium sulphate**, $FeSO_4, (NH_4)_2SO_4, 6H_2O$—is much more stable, and is often used in standardising solutions of potassium permanganate (p. 453).

Ferrous sulphide, FeS (p. 215), is obtained as a black precipitate when solutions of ferrous or of ferric salts are treated with ammonium sulphide (not with hydrogen sulphide, p. 220); with ferrous salts a simple double decomposition occurs,

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4;$$

but ferric salts are first reduced to ferrous compounds,

$$Fe_2(SO_4)_3 + (NH_4)_2S = 2FeSO_4 + (NH_4)_2SO_4 + S.$$

FERRIC COMPOUNDS.

The ferric salts are usually prepared by oxidising the ferrous salts with chlorine, nitric acid, &c., and are generally yellow; they may be reduced to ferrous salts with nascent hydrogen (p. 341).

Ferric oxide, Fe_2O_3, may be obtained by igniting ferric hydroxide (or ferrous sulphate, p. 491). it is a reddish-brown solid (hæmatite, rouge), and is only slowly attacked by concentrated hydrochloric acid.

A mixture of ferric oxide and granulated aluminium is extensively used under the name of *thermite* for the production of a high temperature in certain metallurgical operations. When this mixture is lighted with a 'fuse' of magnesium ribbon a very vigorous reaction occurs (p. 443),

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3,$$

and the heat development is so great that the iron and alumina both melt. Hence, with the aid of thermite, steel rails, &c., may be welded together as they lie, and all sorts of repairs to iron and steel work may be carried out without the aid of a furnace.

Ferric hydroxide, $Fe(OH)_3$, is formed as a reddish-brown flocculent precipitate on a solution of sodium or ammonium hydroxide being added to a solution of a ferric salt,

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

The precipitate is soluble in a solution of ferric chloride; and when this product is submitted to dialysis, a 'colloidal solution' (p. 327) of ferric hydroxide is obtained.

Ferric hydroxide is a relatively weak base, and does not give salts with very weak acids such as sulphurous and carbonic acids.

Ferric chloride, $FeCl_3$, may be prepared by heating iron in a stream of dry chlorine; the product is readily volatile (b.p. about 280°), and condenses in dark, lustrous crystals. It is readily soluble in water, giving a brownish-red solution which contains basic salts formed by hydrolysis, and the colour of which becomes more intense on warming, owing to the further formation of such basic salts.

Solutions of ferric chloride may be obtained by dissolving the hydroxide in hydrochloric acid, by passing chlorine into a solution of the ferrous salt, or by oxidising the latter with nitric, in presence of hydrochloric, acid,

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + NO + 2H_2O.$$

On evaporation, such solutions give yellow, crystalline, hydrated salts of variable composition.

Ferric sulphate, $Fe_2(SO_4)_3$, prepared by dissolving the hydroxide in sulphuric acid, gives **ferric alums** with sulphates of the type X_2SO_4 (p. 616).

Ferric phosphate, $FePO_4$, is met with in qualitative analysis as a pale-yellow flocculent precipitate, which, like the phosphates of chromium and aluminium, is insoluble in acetic acid.

Iron pyrites, FeS_2 (pp. 221, 287), is an important iron compound, and may be regarded as a derivative of tervalent iron; obviously, however, its constitution, possibly expressed by the formula $S:Fe{\cdot}S{\cdot}S{\cdot}Fe:S$, does not correspond with that of ferric oxide.

Iron compounds are easily detected in the laboratory, and ferrous are easily distinguished from ferric salts with the aid of a solution of sodium or ammonium hydroxide or a solution of potassium ferricyanide (see below).

Potassium ferrocyanide, $K_4Fe(CN)_6, 3H_2O$, and *potassium ferricyanide*, $K_3Fe(CN)_6$, are described elsewhere.* The ferrocyanide may be obtained in the laboratory by treating ferrous hydroxide with potassium cyanide (p. 679),

$$Fe(OH)_2 + 6KCN = K_4Fe(CN)_6 + 2KOH,$$

and the ferricyanide by passing chlorine into a solution of the ferrocyanide,

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

Potassium ferrocyanide and ferr*ic* salts, and potassium ferr*i*cyanide and ferr*ous* salts, when mixed together in aqueous solution, give a blue precipitate (Prussian blue, Turnbull's blue); but potassium ferr*i*cyanide and a ferr*ic* salt do not give a precipitate.

NICKEL, Ni; AT. WT. 58·7.

Nickel occurs in meteorites, and generally associated with cobalt. It is found in a number of ores as sulphide, arsenide, and silicate.

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* *Organic Chemistry* (Perkin and Kipping; W. & R. Chambers, 7s. 6d.).

Some of the more important ores, such as *garnierite*, are complex silicates of nickel, iron, calcium, and magnesium: the *arsenide*, NiAs, is a copper-red mineral known as *kupfernickel.*

The extraction of nickel from these ores, and especially its separation from cobalt, were until comparatively recently very troublesome operations; but an important discovery by L. Mond has overcome these difficulties.

When carbon monoxide is passed over finely divided nickel, heated at about 55°, combination occurs, and **nickel carbonyl,** $Ni(CO)_4$, distils as a colourless, highly refractive, poisonous liquid (b.p. 43°), which is readily decomposed at about 200° into nickel and carbon monoxide. Cobalt does not combine with carbon monoxide under the above conditions.

Based on these principles, the following process is now employed for the commercial preparation of nickel. The ores are first 'roasted' if they contain sulphides and arsenides, in order to convert these compounds into the oxide; they are then heated at about 400° in a mixture of carbon monoxide and hydrogen (water-gas) until the oxide is reduced to the finely divided metal. When reduction is complete the temperature is lowered to about 55°, and the nickel carbonyl, which is then produced, is passed into chambers heated at about 200; at this temperature the compound is rapidly decomposed into metal and carbon monoxide, and the metal is deposited in a coherent, highly lustrous form.*

Nickel is a silvery metal of sp. gr. 8·8, and melts at about 1455°. It does not rust appreciably; for this reason, and also on account of its beautiful lustre, it is used in plating iron and other metals. It is also used for the preparation of alloys, such as German silver (nickel 25, zinc 25, and copper 50 per cent.), and in the manufacture of nickel steel (p. 700).

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* Iron combines with carbon monoxide at high temperatures and pressures, giving **iron pentacarbonyl,** a volatile yellow liquid of the *molecular* formula $Fe(CO)_5$. This liquid decomposes on exposure to light, giving a yellow solid, $Fe_2(CO)_9$, and by heating a solution of this solid at 95°, **iron tetracarbonyl,** $Fe(CO)_4$, a green crystalline compound of complex *molecular* formula, is obtained.

Cobalt combines with carbon monoxide *under pressure* at 150°, giving

The compounds of nickel are not of great importance. The metal is rapidly acted on by nitric acid, giving the nitrate, but it is only slowly attacked by hydrochloric or sulphuric acid. The anhydrous salts are mostly yellow, but the hydrated crystals and their aqueous solutions are generally green.

Nickel sulphate, $NiSO_4, 7H_2O$, is prepared by dissolving the metal in sulphuric acid, in presence of nitric acid, and then evaporating the solution; it is readily soluble in water, and is isomorphous with other sulphates of the type $XSO_4, 7H_2O$.

Nickel hydroxide, $Ni(OH)_2$, is obtained by precipitation as a light-green flocculent solid, which is converted into **nickelous oxide,** NiO, when it is heated.

The other salts of nickel are also derived from the oxide NiO. A higher oxide, *nickelic oxide*, Ni_2O_3, is known, but it is not basic, and with acids it gives nickelous salts and oxygen or chlorine as the case may be. This oxide is precipitated as a black powder when a nickel salt is treated with sodium hypochlorite, or with bromine and sodium hydroxide, in aqueous solution,

$$2Ni(OH)_2 + NaOCl = Ni_2O_3 + 2H_2O + NaCl.$$

Nickel sulphide, NiS, is formed as a black precipitate on ammonium sulphide being added to a solution of a nickel salt; it is only slowly attacked by hydrochloric acid.

COBALT, Co; AT. WT. 59·0.

This metal is very similar to nickel in its main characteristics, and its principal compounds correspond in type with those of nickel. It may be obtained by reducing its oxide in a stream of hydrogen. It has a reddish lustre, a sp. gr.

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orange crystals of a compound of the molecular formula $Co_2(CO)_8$; this carbonyl decomposes at 60°, giving black crystals of a substance of the empirical formula $Co(CO)_3$. Molybdenum carbonyl, $Mo(CO)_6$, a colourless crystalline substance, is also known.

8·8, and melts at about 1530°. The metal is but little used.*

Cobalt nitrate, $Co(NO_3)_2, 6H_2O$, is obtained in pink crystals when the metal is treated with nitric acid and the solution is then concentrated. The **hydroxide,** $Co(OH)_2$, is formed as a pink precipitate on sodium hydroxide being added to a boiling solution of the nitrate; at ordinary temperatures a bluish precipitate of a basic salt is obtained. **Cobaltous oxide,** CoO, is prepared by heating the hydroxide out of contact with the air; in presence of air cobaltic oxide is also formed.

Cobalt sulphate, $CoSO_4, 7H_2O$, **cobalt chloride,** $CoCl_2, 6H_2O$, and other salts derived from the oxide CoO, are pink in the hydrated form and in solution, but turn blue when they are dehydrated.

Characters written on paper with a dilute (pale-pink) solution of the chloride (*sympathetic ink*) are barely visible, but when the paper is warmed the salt is converted into the more intensely coloured (blue) anhydrous compound.

On sodium hypochlorite, or bromine and sodium hydroxide, being added to a solution of a cobalt salt, **cobaltic hydroxide,** $Co(OH)_3$, is precipitated as an almost black solid. This hydroxide, and the corresponding **cobaltic oxide,** Co_2O_3, are so feebly basic that they do not give rise to stable salts.

Cobalt sulphide, CoS, closely resembles nickel sulphide.

Although nickel and cobalt are so similar chemically in all their simple derivatives, cobalt forms a great number of complex compounds, analogues of which are not obtainable from nickel. Some of these complex cobalt compounds are used in separating cobalt from nickel.

Potassium cobalticyanide, $K_3Co(CN)_6$, a complex salt (p. 591) corresponding with potassium ferricyanide (p. 705), is formed when a solution of a cobalt salt is warmed with excess of potassium cyanide in the air. The *cobaltous cyanide,* $Co(CN)_2$, first produced as a dirty-brown precipitate, combines with potassium cyanide, forming soluble *potassium cobaltocyanide,*

$$Co(CN)_2 + 4KCN = K_4Co(CN)_6,$$

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* The principal ores of cobalt are *cobalt glance,* $CoSAs$ (or CoS_2, $CoAs_2$), and *speisscobalt,* $CoAs_2$.

which then undergoes atmospheric oxidation, giving soluble *potassium cobalticyanide*,

$$4K_4Co(CN)_6 + O_2 + 2H_2O = 4K_3Co(CN)_6 + 4KOH.$$

Potassium cobalticyanide is not acted on by a solution of sodium hypochlorite or hypobromite.

Nickel salts behave like cobalt salts in so far that they give an insoluble cyanide, $Ni(CN)_2$, which combines with potassium cyanide, yielding a soluble salt; but this soluble salt, $Ni(CN)_2, 2KCN$, is not of the same type as potassium cobaltocyanide, and it does not change when its solution is heated in the air. The soluble nickel salt, moreover, is readily and completely oxidised by sodium hypochlorite or hypobromite, giving a precipitate of nickelic oxide; hence by these reactions nickel salts may be detected in presence of cobalt salts, and the two 'metals' may be separated.

Potassium cobaltinitrite, $K_3Co(NO_2)_6$, is obtained in a hydrated form as a yellow precipitate on a solution of a cobalt salt being treated with acetic acid and potassium nitrite; nickel salts do *not* give a precipitate under these conditions, so that this reaction is also utilised in separating these two elements.

PLATINUM AND ALLIED METALS.

The six metals which, together with iron, nickel, and cobalt, comprise Family VIII. of the periodic system (table, p. 720) are generally classed together as the platinum metals, not because they form a natural family, but for convenience, and because in some respects they are similar in their general behaviour.

Family VIII., in fact, is not comparable with any of the other families of the periodic system; it may be regarded rather as consisting of the following three sub-families, in each of which the elements are related to one another in a manner recalling the relationship in other sub-families:

(*a*) Iron	Nickel	Cobalt
(*b*) Ruthenium	Rhodium	Palladium
(*c*) Osmium	Iridium	Platinum.

Thus the members of the iron sub-family resemble one another, and differ from those of the other two sub-families in forming oxides of the type XO_3;* but at the same time it must be admitted that the family valencies are very irregular, and that in consequence the three sub-families are not very sharply defined.

The platinum metals are found alloyed together and with other metals in sandy deposits, especially in the Ural district; but also in California and Australia. They are extracted by first 'washing' the sand, and then treating the residue with aqua regia, whereby most of the metals, but not osmium and iridium, are converted into soluble chlorides. The separation of the different elements from one another is a very troublesome process.

Ruthenium, Ru, is a steel-gray, brittle metal of sp. gr. 12·3, and melts at about 1800°. It is only slowly attacked by aqua regia, but it combines readily with oxygen at a red-heat, giving various oxides (RuO, Ru_2O_3, RuO_2), which are insoluble in acids. When fused with potassium nitrate and potash it gives an unstable salt, K_2RuO_4, derived from the oxide, RuO_3. Perhaps the most interesting ruthenium derivative is the *tetroxide*, RuO_4 **(per-ruthenic anhydride)**, which is formed when potassium ruthenate, K_2RuO_4, is oxidised with chlorine in aqueous solution. This tetroxide sublimes, giving yellow crystals, when it is gently heated, but it decomposes at about 108°. When treated with potassium hydroxide solution it yields potassium ruthenate and **potassium per-ruthenate,** $KRuO_4$, a black, crystalline compound.

Ruthenium unites with chlorine, giving $RuCl_2$ and $RuCl_3$. Derivatives of $RuCl_4$ are also known.

Osmium, Os, is a gray metal of sp. gr. 22·5 (greater than that of any other substance), and melts at about 2500°. It resembles ruthenium in chemical behaviour, and like that metal combines with oxygen at a red-heat. When fused with potash and potassium nitrate it gives potassium osmate, K_2OsO_4, a dark-violet crystalline salt of osmic acid.

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* **Potassium ferrate,** K_2FeO_4, a dark-red, crystalline, unstable compound, is formed when iron powder is heated with potassium nitrate; it is a salt of ferric acid, H_2FeO_4, which is derived from the anhydride, FeO_3, but the free acid and its anhydride are both unknown.

The most interesting and important derivative of osmium is the *tetroxide*, OsO_4, corresponding with RuO_4. This compound is the anhydride of *per-osmic acid*, but is generally known as **osmic acid.** It is formed, and distils over, when osmium is heated in the air, and is also obtained by oxidising the metal with chlorine water or with aqua regia. It forms colourless crystals, boils at about 100°, and has an irritating odour recalling that of chlorine. Its aqueous solution is used in staining biological specimens for microscope work, as the oxide is reduced by the organic matter, giving a deposit of osmium.

Rhodium, Rh, and **iridium,** Ir (sp. gr. 22·4), are not oxidised when they are heated in the air; they are not acted on by aqua regia, but when they are alloyed with platinum they pass into solution. **Iridium tetrachloride,** $IrCl_4$, resembles platinic chloride; but rhodium forms a *trichloride*, $RhCl_3$. Iridium-platinum alloys are harder than platinum, and better resist the action of acids; they are used in preference to pure platinum for the manufacture of crucibles, &c.

Palladium, Pd, is a silvery metal of sp. gr. 9·1, and melts at about 1400°. It resembles platinum in many respects, but differs from it in being attacked by hydrochloric, sulphuric, or nitric acid. It forms stable compounds such as the **oxide,** PdO, and the **chloride,** $PdCl_2$, in which it is bivalent, and also compounds such as the **tetrachloride,** $PdCl_4$, in which it is quadrivalent.

The most interesting property of palladium is that it absorbs (or occludes) as much as about 650 times its own volume of hydrogen when it is heated in this gas at about 95°, and about 370 times its own volume at ordinary temperatures. The whole of the hydrogen is expelled again when the 'alloy' is heated at 100° in a vacuum, and it is believed that the two elements do not combine chemically, but form a solid solution (p. 323).

Platinum, Pt, at. wt. 195·2, has a silvery lustre and a sp. gr. 21·5, which is nearly as great as that of osmium and that of iridium; it melts in the oxy-hydrogen blowpipe flame (at about 1770°). It is not acted on by acids, but with aqua regia it gives a yellow solution of platinic chloride. The hydroxides, sulphides, and cyanides of the alkali metals, many ordinary metals, and some non-metals attack platinum readily at high temperatures, converting it into compounds or into fusible alloys; for this reason such substances must not be heated in platinum vessels. It is also important to avoid the use of a luminous or smoky flame in heating platinum, as the metal unites with, or dissolves, carbon.

Platinic chloride, $PtCl_4$, one of the better-known platinum compounds, is formed when the metal is treated with aqua regia; the product combines with hydrogen chloride, and on the solution being evaporated, brownish-red, hydrated crystals of **chloroplatinic acid,** H_2PtCl_6, are obtained. It is a solution of this compound, commonly called 'platinic chloride,' which is used in the laboratory in testing for potassium (p. 678) and for other purposes. The compound, $PtCl_4$, the true platinic chloride, is obtained by heating the metal in chlorine at about 360°.

Sodium platinichloride, Na_2PtCl_6, is very readily soluble in water.

'*Spongy*' *platinum*, or *platinum sponge*, is obtained by heating ammonium platinichloride (p. 678); ammonium chloride and chlorine volatilise, and metallic platinum remains in a very fine state of division. This form of the metal is much more active than compact platinum, and is an important catalytic agent; thus when a jet of hydrogen or of coal-gas is allowed to impinge on platinum sponge, combination with atmospheric oxygen takes place so rapidly that in a moment the gas ignites.

Platinum black is an even more finely divided form of the metal which is obtained by treating a solution of 'platinic chloride' with zinc or other reducing agents. It is an active catalyst, and also shows to a much greater extent than compact platinum the property of occluding certain gases. The compact metal occludes both oxygen and hydrogen at ordinary temperatures, but only in small quantities, whereas platinum black occludes about 100 times its own volume of oxygen, and an even greater volume of hydrogen.

Platinic chloride is decomposed by sodium hydroxide solution, and on excess of acetic acid being added to the product, **platinic hydroxide,** $Pt(OH)_4$, is obtained as a reddish-brown precipitate, which forms soluble salts with the alkali hydroxides.

Platinous chloride, $PtCl_2$, is formed when platinic chloride is heated at 200°. When treated with excess of potassium cyanide it is converted into **potassium platinocyanide,** $K_2Pt(CN)_4$, and with barium cyanide it gives **barium platinocyanide,** $BaPt(CN)_4$; the latter forms hydrated crystals, $(4H_2O)$, which are strongly fluorescent, and which are used in coating screens for X-ray work, because they render visible the Röntgen rays.

CHAPTER LXIII.

The Classification of the Elements and the Periodic System.

In describing the more important elements, attention has been directed to the existence of certain relationships which render it possible to classify these elements into natural families, and in most cases the nature of this relationship has also been briefly discussed. It is now desirable to deal comprehensively with this subject, and to explain the system of classification which has been adopted.

The first attempt to classify the elements was a very simple one; they were divided into metals and non-metals. At first this division was based entirely on a consideration of their physical properties (p. 35); later, elements were discovered which differed from the common metals in physical properties, but yet resembled the latter in chemical behaviour; it was then recognised that the chemical properties of an element must be taken into consideration if the division into metals and non-metals is to be maintained (pp. 253–255). At the present day the elements are still divided into these two groups.

A metal forms at least one basic oxide; its corresponding chloride is not hydrolysed by water (p. 428); it displaces hydrogen from acids; it does not give volatile hydrides; it is electro-positive.

A non-metal forms only acidic oxides; its chlorides are hydrolysed by water; it does not displace hydrogen from acids; it gives one or more volatile compounds with hydrogen; it is electro-negative.

On this basis it is possible to place nearly all the elements in one or other of the two groups; a few elements, however, notably arsenic and antimony, present some difficulties and seem to belong almost equally to the metals and to the non-metals.

Clearly this division of some 80 elements into two groups only, does not carry the matter very far, and the next noteworthy step in advance was the classification of a number of the elements into various small families, according to their chemical behaviour. Thus the three elements chlorine, bromine, and iodine were grouped together on account of their similarity in properties; so also were calcium, strontium, and barium; iron, nickel, and cobalt; and so on.

In 1827 Döbereiner drew attention to the fact that in many of these families of three elements the atomic weights of the elements showed an interesting relationship; in some families the atomic weight of the second member was, roughly, the mean of those of the other two, while in other families the atomic weights of the three elements were almost of the same magnitude. Such families, of which examples are given below, were known as Döbereiner's triads:

Chlorine . .	35·5	Calcium . .	40·1	Iron . .	55·8
Bromine . .	79·9	Strontium .	87·6	Nickel . .	58·7
Iodine . .	126·9	Barium . .	137·4	Cobalt . .	59·0
$\frac{35{\cdot}5+126{\cdot}9}{2}=81{\cdot}2$		$\frac{40{\cdot}1+137{\cdot}4}{2}=88{\cdot}8$			

This classification into a number of families, accompanied by a recognition of some relationship between the *properties* of an element and its *atomic weight*, was a great advance; but the scheme failed to embrace all the known elements in a systematic manner.

About 1864 a very important discovery was made by Newlands—namely, that there is a relation between the properties of an element and its atomic weight of such a character that *when the elements are arranged in the order of their increasing atomic weights, elements having similar properties recur at fixed intervals.* Taking the atomic weights accepted in those days, Newlands arranged some of the elements in the order of these magnitudes, and pointed out that the 8th element was similar to the 1st, the 9th to the 2nd, the 10th to the 3rd, and so on. As this similarity recurred at every 8th element, just as the 8th note in the musical scale is an octave to the 1st, he supposed that the relationship accorded with some natural law, and termed his discovery '*the law of octaves.*'

This discovery of Newlands was extended to all the elements and greatly developed in various directions by Mendeléeff and L. Meyer; the system thus devised, based, as was that of Newlands, on the atomic weights of the elements, is now known as the *natural system*, or, since the properties of an element are periodic functions of its atomic weight, the *periodic system.*

In order to explain this system, the symbols and atomic weights (*in whole numbers*) of 24 of the elements are set out in the following horizontal rows:

He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al
4	7	9	11	12	14	16	19	20	23	24	27
Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn
28	31	32	35	38(?)	39	40	44	48	51	52	55

Except that hydrogen (at. wt. = 1) is omitted, this list includes *all* the known elements with atomic weights less than 56, and the elements follow one another strictly in the order of their atomic weights.

Now a study of this very simple arrangement brings out the fact that although the properties of any two successive elements are generally very different, elements which are related to one another are met with at fixed intervals or after fixed *periods;* thus the 1st element is similar to the 9th * and the 17th, the 2nd to the 10th and 18th, and so on. In fact the physical and chemical properties of the elements, and those of all their compounds, are periodic functions of the atomic weights.

If, then, the horizontal rows given above are divided into the three *periods* (each containing 8 elements) of which they consist, and these periods are placed vertically one below the other, elements in corresponding positions in these periods become grouped together in *vertical series:*

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl
Ar	K	Ca	Sc	Ti	V	C	Mn

Thus the three elements, helium, neon, and argon, which are very closely related, form a natural family; similarly with lithium, sodium, and potassium; with beryllium, magnesium, and calcium, and so on. In order to obtain this obviously satisfactory classification, hydrogen only, as already stated, is omitted.

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* Not to the 'octave,' as in Newlands's list, because of the discovery of other elements since Newlands's time.

In the list of elements which follow manganese in the order of increasing atomic weights (which, except in the case of that of Ni, are given in whole numbers), the next eight would be,

Fe	Ni	Co	Cu	Zn	Ga	Ge	As
56	58·7	59	64	65	70	72	75

But if this row were placed under the third period given above, iron would fall into the family of rare gases (He, Ne, Ar), nickel would be classed in the family of the alkali metals (Li, Na, K), and in fact *all* the eight elements in this row would fall into families with the members of which they have absolutely no relationship. If, however, iron, nickel, and cobalt are placed temporarily aside, and the period of 7 elements, starting from copper (Cu), and consisting of

Cu Zn Ga Ge As Se Br,

is placed under the third of the above periods in such a way that copper falls under potassium, *leaving a gap under argon*, then the arrangement is much more satisfactory, and the elements following this period also fall into suitable positions.

These illustrations will suffice to show that the arrangement of the elements in the order of their increasing atomic weights leads to their classification into natural families, provided that certain elements are *temporarily* excluded from the periods, and that certain *gaps* are left, where to do otherwise would obviously upset the whole system.

If the classification be continued on the lines indicated, the atomic weights being strictly adhered to for the *order* in which the elements are taken, all the elements* may be classed in such a way that their mutual relationships are exhibited.

*** Some rare and little-known elements have been left out of consideration.**

One arrangement of this kind is shown on the chart facing the last page of the index.

Helium (He) being taken as the starting-point, there first come the two periods, each consisting of 8 elements, which have already been referred to; these periods are placed centrally, and are called *short periods;* the elements of which they consist are sometimes called *typical elements.*

The third (short) period of 8 elements is placed on the left of the chart, followed by Fe, Ni, Co, and the fourth (short) period (of 7 elements), commencing with copper, is placed on the right. The whole of this horizontal row, comprising one short period of 8 elements, Fe, Ni, Co, and one short period of 7 elements, or 18 elements in all, is termed a *long period.*

A second long period of the same kind, beginning with Kr, then follows, but this period is incomplete; a blank or gap is left under manganese (Mn), because if this were not done the obviously more suitable arrangement of all the succeeding elements would be disturbed. It may be stated at once that, for reasons given later, it is conceivable, or even probable, that this and other gaps may at some future time be filled by elements which have not yet been discovered.

A third long period begins with X, but is very fragmentary; a fourth is very incomplete, and a fifth contains only three elements. It should be understood that although (omitting Yb) there would be room for all the elements of the fourth long period in the third, the great difference between the atomic weight of Ce (140) and Ta (181), compared with the usual difference (2–4 units) between any two successive atomic weights, seems to show that the arrangement given in the chart is to be preferred.

When arranged in this way all the elements fall naturally into families.* Each of these families consists of all those

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[*] The term 'family' is used in preference to 'group' in order to avoid confusion with the 'groups' into which metals are classed in qualitative analysis.

elements which occupy *corresponding* positions in the short periods. Thus, all the short periods, each of which consists of *eight* elements, being taken, the first members are He, Ne, Ar, Kr, X; these elements are closely related and form a natural family (Family 0). These five elements being taken away, all the short periods now consist of *seven* elements (unless the periods are incomplete), and are comparable. If, then, the *first* members of *all* the small periods of seven elements are classed together, and similarly all the *second* members, and so on, seven more families are obtained. These families are numbered I. to VII. respectively; all the elements between the two vertical lines in the chart are classed together as Family VIII.

These eight families are shown on p. 720, where the relative positions in the chart of the different members (and of the gaps) are also indicated.

Although all the elements forming any one of these families are related to one another, the relationship is of such a character that the family may sometimes be divided into two sub-families. Thus of the eight elements in Family I., Li, Na, K, Rb, Cs, are far more closely related to one another than to Cu, Ag, Au, and these three elements are more closely related among themselves than to Li, Na, K, Rb, Cs (the alkalis). Similarly, Family II. may be divided into the sub-families Ca, Sr, Ba (the alkali-earth metals), and Be, Mg, Zn, Cd, Hg; but it is not very easy to decide whether Be and Mg should be classed with Ca, Sr, Ba, or with Zn, Cd, Hg, as they are almost equally related to both of these series. Families III. and IV. present similar difficulties as regards division into sub-families; but in Families V., VI., and VII. the relationship between the typical elements (p. 718), and those occupying corresponding positions on the right-hand side of the *long* periods (see chart), becomes closer and closer in passing from Family V. to Family VII. In Family VII., for example, F and Cl are very closely related to Br and I, but are only very distantly related to Mn, and in Family VI., O and S are

0.	I.		II.		III.		IV.		V.		VI.		VII.		VIII.		
He	Li			Be		B		C		N		O		F			
Ne	Na			Mg		Al		Si		P		S		Cl			
Ar	K		Ca		Sc		Ti		V		Cr		Mn		Fe	Ni	Co
		Cu		Zn		Ga		Ge		As		Se		Br	—	—	—
Kr	Rb		Sr		Y		Zr		Nb		Mo		—		Ru	Rh	Pd
		Ag		Cd		In		Sn		Sb		Te		I	—	—	—
X	Cs		Ba		La		Ce		—		—		—		—	—	—
		—		—	Yb			—	Ta		W			—	Os	Ir	Pt
		Au		Hg		Tl		Pb		Bi			—		—	—	—
			Ra				Th				U						

very much more closely related to Se and Te than to Cr and the elements below Cr.

This division into sub-families is indicated in the table (p. 720) by printing the symbols of the elements of the sub-families in vertical lines. Thus Li and Na are printed directly above K, Rb, Cs; similarly, F and Cl are printed vertically over Br and I, and so on.

In this volume (Part II.) the families have been taken in the order VII. to 0, and in every case the sub-families comprising elements on the right-hand side have been taken before those comprising elements on the left-hand side of the chart; Family VIII. has been taken last.

If the nature of the relationship between the various members of a natural family be next considered, perhaps the most important fact is that all the members have the *same valency.* Before discussing this matter, it must again be pointed out that the valency of an element may be variable, in which case its valency towards hydrogen may be different from its valency towards oxygen; therefore, in speaking of valency, it is generally necessary to state to which of these standards the property is referred.

Hydrogen being taken as the standard, or where no hydrogen compound of the element is known, one of the univalent halogens, the *family valency* gradually rises from 0 (at Family 0) to a maximum of four, and then gradually falls to one, in passing from Family 0 to Family VII. Instead of the families as a whole, the elements of any short period may be considered, as each of these elements is typical of its own family. In the first small period, then, the molecular formulæ of the hydrides or (where hydrides are unknown*) of the chlorides of these elements are as follows:

$$\mathrm{LiCl} \cdot \mathrm{BeCl_2} \quad \mathrm{BH_3} \quad \mathrm{CH_4} \quad \mathrm{NH_3} \quad \mathrm{OH_2} \quad \mathrm{FH}.$$

---

* **Although hydrides of lithium and of sodium are known, they are not typical compounds, and therefore are not considered here.**

Similarly, the formulæ of the hydrides (or chlorides) of the elements of the second short period are:

$$NaCl \quad MgCl_2 \quad AlCl_3 \quad SiH_4 \quad PH_3 \quad SH_2 \quad ClH,$$

so that the following connection holds:

Family	0.	I.	II.	III.	IV.	V.	VI.	VII.
Valency towards H (or Cl)	0	1	2	3	4	3	2	1

The valency towards a halogen is not always the same as the valency towards hydrogen; thus in Families V. and VI. some of the elements are quinquevalent and sexvalent respectively in their highest chlorides.

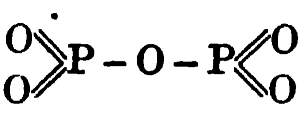
As regards the family valency towards oxygen, there is the difficulty that most of the elements form several oxides, and have several valencies towards this element, and therefore, in order that any comparison may be made, some particular class of oxide must be chosen. The study of this matter has shown that the relationships are most clearly brought out by considering the valency of the element in its highest salt-forming oxide, a salt-forming oxide being defined as either an anhydride, or a basic oxide, from which corresponding salts are derived. Now the formulæ of the highest salt-forming oxides of the elements of the first two short periods are as follows:

$$\begin{array}{llllllll} - & Li_2O & BeO & B_2O_3 & CO_2 & N_2O_5 & - & - \\ - & Na_2O & MgO & Al_2O_3 & SiO_2 & P_2O_5 & SO_3 & Cl_2O_7. \end{array}$$

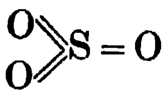
From these formulæ it will be seen that there is a regular change in valency in passing from Family 0 to Family VII., and that this change is a continuous increase by one unit for every family.

That the valencies of the elements in these periods (and therefore in the families) rise continuously from 1 to 7 is more clearly expressed in the structural formulæ of these oxides; thus the oxides of the elements of the second small period may be respectively represented by the formulæ,

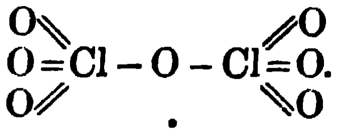
$Na-O-Na \quad Mg=O \quad O=Al-O-Al=O \quad O=Si=O$



$\begin{matrix}O\\ \\O\end{matrix}\!\!>\!P-O-P\!<\!\!\begin{matrix}O\\ \\O\end{matrix}$



$\begin{matrix}O\\ \\O\end{matrix}\!\!>\!S=O$



$\begin{matrix}O\\O\\O\end{matrix}\!\!=\!Cl-O-Cl\!=\!\!\begin{matrix}O\\O.\\O\end{matrix}$

This gradual change in valency is also well brought out by a study of the hydroxides of the elements. Taking those which correspond with the highest salt-forming oxides, the following series is obtained:

$$Na(OH) \; Mg(OH)_2 \; Al(OH)_3 \; Si(OH)_4 \; P(OH)_5 \; S(OH)_6 \; Cl(OH)_7.$$

Some of these hydroxides, it is true, are unknown in the free state, but of these some probably exist in aqueous solution, and the remainder are known in the form of their derivatives (pp. 469, 493, 574, 584).

It is thus clear that as regards valency the system of classification under discussion brings out the periodic variation of this property; but the valency of most elements is so variable, so dependent on the standard by which it is measured, and also on the conditions under which it is determined, that the generalisations given above may not in all cases hold good. For this and other reasons the periodic system is not of great assistance to the student until his knowledge of chemistry is well advanced.

The next point to be considered is that although the members of a natural family are similar in properties, all their properties and likewise those of their corresponding compounds vary in a regular manner with increasing atomic weight; this regularity is even more marked when the comparison is restricted to the members of a sub-family. Thus, taking the sub-family of the halogens, the regularities already pointed out (pp. 423–428) are very clearly defined. Corresponding gradations are observed in other sub-families, no matter what property is considered, and the relation between properties and atomic weight is thus brought out in another way.

As further instances of this gradual change in the properties of the members of a sub-family, the following data may be given:

The specific gravities and melting-points of the alkali metals (Sub-Family I.) are:

	Li	Na	K	Rb	Cs
Specific gravity at 15°	0·53	0·97	0·87	1·5	1·9
Melting-point	185°	97°	60°	39°	27°

The specific gravities and the solubilities in water of the sulphates of the alkali earth metals are:

	$CaSO_4$	$SrSO_4$	$BaSO_4$
Specific gravity *	2·9	3·7	4·5
Parts of water required to dissolve one part of sulphate	520	6800	400,000

The heats of formation (p. 337) of the chlorides of some of the metals of Family II. are:

	$MgCl_2$	$ZnCl_2$	$CdCl_2$	—	$HgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
Large calories †	151	97	93	—	54·5	170	185	194

In all these cases the gradation is clearly defined; but, as will be seen from the first example, there is sometimes a break in passing from the typical elements to those of the long periods. This is by no means uncommon (p. 649).

A study of the chart facing the last page of the index brings out another very interesting result of the classification of the elements here shown—namely, that all the non-metals or electro-negative elements are grouped together in such a way that they may be fairly sharply divided from the metals. This is indicated by the discontinuous line.........in the chart. All the non-metals are situated on the right of, or above, this line; owing to the difficulty of deciding whether arsenic and antimony should be classed as metals or as non-metals, the line is duplicated as regards these elements. Not only are the metals thus grouped together, but all the more strongly electro-positive metals (the alkalis and the metals of the alkali-earths) are also brought into close proximity at the extreme left of the table; similarly, the magnetic elements (Fe, Ni, Co),

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* Varies with the crystalline form.

† Compare footnote, p. 346.

the best three conductors of heat and electricity (Cu, Ag, Au), and so on, are found to be neighbours in the system.

The periodic system has proved to be of very great service in fixing the ratio between the equivalent and the atomic weight of an element, and also for correcting or checking atomic weights which might not be trustworthy. Thus the determination of the equivalent of beryllium gives $E = 4{\cdot}5$, so that the atomic weight of the element is nE. From certain resemblances between beryllium and aluminium it was at first thought that the former, like the latter, must be a tervalent element, in which case $n = 3$, and the atomic weight of beryllium would be 13·5. But there was no place in the periodic system for an element of atomic weight 13·5 between carbon (at. wt. 12) and nitrogen (at. wt. 14). On the other hand, there was a vacancy between lithium (at. wt. 7) and boron (at. wt. 11). It was concluded, for this reason alone, that beryllium must be a bivalent metal of atomic weight 9. Subsequently the vapour density of beryllium chloride was determined, and it was found that the molecular formula of this chloride is $BeCl_2$; this result proved that the element is bivalent, that its atomic weight is 9, and that the deduction based on the periodic system was a sound one.

Similar arguments were applied in fixing the relation between the equivalent and the atomic weight in the cases of indium, uranium, and several other elements.

As an instance of the usefulness of the periodic system for the correction of atomic weights, the cases of osmium, iridium, and platinum (Family VIII.) may be mentioned. The earlier determinations gave Pt = 187·4, Ir = 198, Os = 199·7; but when placed in the periodic system in this order platinum and osmium did not show relationships in conformity with the system. Hence new atomic weight determinations were made, with the result that the order became Os = 191, Ir = 193, Pt = 195, an order which brought all the elements into more suitable positions.

At the present time there are two elements to which positions strictly in accordance with their atomic weights cannot be assigned. *Tellurium and argon appear to have* atomic weights *greater* than those of iodine and potassium respectively, and therefore should *follow* and not (as printed in the chart) precede the elements last named. But if tellurium were put after iodine, and argon after potassium, all these four elements would be pushed into families in which, obviously, they would be completely out of place. For these reasons many determinations of the atomic weight of tellurium have been undertaken, but so far the value remains higher than that of iodine, and no satisfactory explanation of this anomaly has been advanced. The case of argon has not been so fully examined.

Since all the properties of an element depend on the magnitude of the atomic weight of the element, which magnitude determines the position of the element in the periodic system, it follows that the properties of an element may be *predicted* from its atomic weight. Now in the chart many gaps or vacant spaces have been left for reasons already stated, and it has been mentioned that these gaps may be ultimately filled by hitherto undiscovered elements. In 1871 there were several more gaps in the table than there are at present, and in order to test the value of the 'periodic law' Mendeléeff predicted the properties of some of these unknown elements. One case showing the extraordinary accuracy of his predictions may be given. Just before arsenic (As, 75), in the place now filled by germanium (Ge, 72), there was then a gap. Mendeléeff predicted that the element which should fill that gap (and which he called *eka-silicon*) would have an atomic weight of nearly 72; that it would form a higher oxide, XO_2, and a lower oxide, XO; a liquid chloride, XCl_4, which would boil at about 90° and have a sp. gr. about 1·9; the sp. gr. of X would be about 5·5, and that of XO_2 about 4·7.

In 1886 the metal now called germanium was discovered by Winkler. Its atomic weight was found to be 72·3; it forms an oxide, GeO_2, an oxide, GeO, and a liquid chloride which boils at 86°, and has a sp. gr. 1·89; the sp. gr. of Ge is 5·47, and that of GeO_2 4·7. These and other properties of the element discovered by Winkler proved it to be Mendeléeff's 'eka-silicon,' and the generalisation known as the periodic law was thus proved to be a most important advance in knowledge.

THE ATOMIC VOLUME CURVE.

The regular and periodic change in the valencies of the elements as their atomic weights increase may be taken as an example of what is observed when any other property of the elements is studied. As a further instance, the specific gravities of the elements in the solid or liquid state may be considered.* The following data, relating to the elements of the first long period, clearly show that the specific gravity gradually rises from a minimum at the beginning of the long period to a maximum (at Cu), and then gradually falls to a minimum at the end of the long period:

Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe
—	0·87	1·6	2·5	3·6	5·5	6·7	7·5	7·8
Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
8·7	8·6	8·8	7·1	6·0	5·5	5·6	4·8	3·1

Instead of the specific gravity (the relative weight of unit volume), the reciprocal of this value, or the *specific volume* (the relative volume occupied by unit weight), may be studied with, of course, similar results; but the periodic variation is much more clearly brought out by considering the (relative) *atomic volumes* of the elements. The atomic volume is the volume in c.c. occupied by the gram-atom of an element, and $\text{At.Vol.} = \frac{\text{At.Wt.}}{\text{sp. gr.}}$; the atomic volumes, therefore, represent the *relative* volumes occupied by the atoms of the elements in the solid or liquid state.

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* It should be noted that the specific gravity depends not only on the temperature, but may also vary very considerably with the mechanical treatment and method of preparation of the element; as the given values refer to different temperatures, and as the physical conditions of the elements may not be strictly comparable, slight irregularities are only to be expected.

If, the atomic weights being taken as abscissæ and the atomic volumes as ordinates, a curve is drawn in the usual manner, this curve (the *atomic volume curve*) brings out the periodic variation of the properties of the elements in a most striking way.

The curve is given at the end of this volume, and its careful examination will prove a most interesting study. Among the many important relationships which are thus revealed the following may be particularly noted:

Each of the first two U-shaped sections of the curve corresponds with one of the short periods, while each of the following sections corresponds with one of the long periods; the 'missing' portion of the curve following Ce may be continued in imagination to Ta in a form similar to the corresponding portion of the preceding complete section, and in like manner the 'missing' portion following Bi may be imagined as rapidly rising to a maximum before it falls again to Ra.

Elements which are closely related in properties occupy corresponding positions on the curve. Li, Na, K, Rb, Cs, all occupy the maxima. F, Cl, Br, I, all occupy ascending portions immediately before the maxima. The electro-positive elements (i.e. the metals) follow one another without a break from the maxima until some distance past the minima; the electro-negative elements (i.e. the non-metals) follow one another on the rapidly ascending portions of the sections. The chemical activity of an element is closely related to its atomic volume; those elements having large atomic volumes are, so far as comparisons can be made, more active than those having small atomic volumes.

The periodic change in the properties of the *elements* as the atomic weights increase is in many respects similar to the periodic change, with increasing molecular weight, in the properties of the *compounds* of various homologous series. Thus in the case of the following substances—and the list could be greatly extended—similar properties recur at definite periods, and the whole arrangement recalls that of the periods of the elements:

CH_4	$H\cdot CHO$	$CH_3\cdot OH$	$H\cdot COOH$	$(CH_3)_2O$	$(CH_3)_2CO$
C_2H_6	$CH_3\cdot CHO$	$C_2H_5\cdot OH$	$CH_3\cdot COOH$	$(C_2H_5)_2O$	$(C_2H_5)_2CO$

It is conceivable, therefore, that the present elements, like the above compounds, are all composed of a relatively small number of different forms of matter, *possibly even of one only.*

Such a view was put forward as long ago as 1816 by Prout, who suggested that the elements might all be composed of hydrogen matter (Prout's hypothesis), in which case their atomic weights should all be simple multiples of that of hydrogen; but the actual values of the atomic weights of many elements, some of which have been determined with great accuracy, do not admit of this possibility.

Nevertheless it is still conceivable that all the elements may have originated from one form of matter, and the wonderful facts which have been brought to light by the discovery of the radio-active 'elements' lend strong support to such a conclusion.

CHAPTER LXIV.

Radio-Activity.

In 1896, almost immediately after the discovery of the Röntgen- or X-rays, the study of certain fluorescent substances, more especially certain salts of uranium, led Becquerel to the detection of another kind of radiation.[*] He found that all uranium salts had a pronounced action on a photographic plate even when they were separated from this plate by thin sheets of metal. This property is known as *radio-activity.*

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[*] The important work of Crookes and others preceding this discovery cannot be described here.

The radio-active uranium salts had further the remarkable property of enormously increasing the electrical conductivity of air, so that when they were brought into the vicinity of a charged gold-leaf electroscope, the charge immediately escaped and the leaves fell together.

Shortly after Becquerel's discovery, Mme. Curie found that thorium compounds likewise possessed radio-activity. Further, that several ores of uranium, notably the *pitch-blendes,* were far more radio-active than the most active uranium compound, or even than uranium itself. From this most important fact she concluded that radio-activity was not a property of uranium or of its salts, but of some new element which was contained in those substances as impurity.

M. and Mme. Curie were then led to attempt the isolation of this unknown element from pitch-blende, a mineral which, in addition to oxides of uranium, contains barium, bismuth, and a large number of other elements (some twenty or more) in a combined form. By suitable processes, they obtained from this mineral a strongly radio-active preparation of a bismuth compound, which they called 'radio-active bismuth,' and a strongly radio-active preparation of a barium compound, which they called 'radio-active barium.' From the latter they ultimately isolated a salt of a new 'element,' **radium,** and from the former, but not in a state of purity, a salt of a new 'element,' **polonium.**

The quantity of radium obtained from a rich sample of pitch-blende is only about 1 part from 10 millions of the ore, and that of polonium about $\frac{1}{500}$ of this amount.

Radium, Ra, at. wt. 226·4, has hitherto been isolated in the pure state only in the form of *radium chloride,* $RaCl_2$, and the corresponding *bromide,* $RaBr_2$. Only a few grams of these salts have been prepared up to the present time (1910), and their price is several thousand pounds sterling.

The ordinary chemical properties of radium (if the term ordinary can be used in relation to such an extraordinary substance) resemble those of barium; but in addition to these, radium, in the form of its *salts*, shows others of a most astonishing character.

It decomposes water and many other 'stable' compounds, converts oxygen into ozone, colourless into red phosphorus, and diamond into graphite. It colours glass or porcelain vessels in which it is contained, and in fact has an action of some kind on nearly all substances, inanimate and animate.

Its radio-activity (that is to say, its effect on a photographic plate) is more than a million times greater than that of any uranium compound. Its power of rendering the air a conductor (or of *ionising* the air) is so intense that by this property 10^{-12} gram of radium may be detected, a quantity far smaller than that which can be detected with the aid of the spectroscope in the case of any element (p. 686).

Further, a radium salt maintains itself continuously at a temperature a few degrees higher than that of its surroundings—*that is to say, it continuously generates heat; the* quantity of heat which it gives out is actually about 118 calories per hour per gram of radium.

The examination of the rays emitted by radium has shown that these are of three kinds, which are distinguished as the α-, β-, and γ-rays respectively. They all have, but to different extents, the property of rendering luminous and fluorescent substances such as barium platinocyanide (p. 713), zinc sulphide, and willemite (zinc silicate).* They differ further not only in their photographic and ionising effects, but also in penetrating power and in the nature and extent to which they undergo deviation from their course in a magnetic or electrostatic field.

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* This property is beautifully shown in the spinthariscope, an inexpensive instrument devised by Crookes. The rays from an almost inconceivably small quantity of a radium salt fall on a screen of zinc sulphide, which is then seen to give brilliant momentary flashes of light as it is bombarded by the α-rays (helium particles).

The α-rays are most active in causing the ionisation of the air. Their photographic action is slight, and they have little penetrating power, being completely stopped even by thin layers of solids, such as a sheet of paper, as well as by liquids and by thicker layers (1 inch) of air. They are only slightly deflected in a magnetic field, and from their behaviour it is concluded that they consist of positively charged particles.

The β-rays affect a photographic plate very strongly. They have a 100 times greater penetrating power than the α-rays, and can pass through thin plates of certain metals. They are deflected in a magnetic field to an extent about 1000 times greater than are the α-rays, and in an opposite direction. From their behaviour it is concluded that they consist of negatively charged particles (negative electrons) which, according to J. J. Thomson, have a mass only $\frac{1}{2000}$ of that of an atom of hydrogen.

The γ-rays are photographically active, and resemble the X-rays. They have a penetrating power 100 times greater than that of the β-rays, and are not completely absorbed even by thick sheets of metals—as, for example, by a leaden plate 7 cm. in thickness.

Radium compounds continuously evolve a radio-active gas which is called the radium *emanation*. This emanation is produced in quantities so minute that only about 0·6 cubic millimetre (at N.T.P.) can be obtained from 1 gram of radium, and yet it has been found possible to liquefy the gas (Rutherford and Soddy), and to determine its boiling-point, freezing-point, and many other physical properties.

When the radium emanation is first produced it loses energy in the form of heat at a greater rate even than does an equal weight of radium; it is also highly radio-active, but emits α-rays only. After some time it begins to give β- and γ-rays; but the emanation is unstable, and in the course of four days its activity is reduced to one-half its original value, while at the end of a month its radio-active properties, have practically disappeared. The gas which then remains contains *helium*.

The formation of helium from radium is a fact of profound importance, from which it must be concluded that certain forms of matter—whether they should be called elements or not is merely a question of definition—are capable of undergoing spontaneous 'decomposition,' although in other respects they may be regarded as elements; the behaviour of radium, and the further facts mentioned below, seem therefore to afford strong grounds for believing that even the ordinary *elements may possibly be transformed one into another.*

This startling inference is already supported by various facts. Uranium, which heretofore was regarded as an ordinary element, is capable of undergoing 'decomposition.' Salts of uranium which have been freed from radium do not exhibit radio-activity; when, however, they have been kept for some time they again become radio-active owing to the presence of radium. Uranium, therefore, gives rise to radium, and the latter then undergoes change, giving an emanation which contains, and gradually passes into, helium.

These remarkable transformations are by no means the only ones which occur. From the results of experiments, which cannot be described here, it is concluded that various unstable substances are produced successively, not only in the formation of radium from uranium, but also in the decay or 'decomposition' of the radium emanation.

Thus the transformation of uranium into radium is supposed to occur as follows:

Uranium → Uranium X → Ionium → Radium;

but in the disintegration of radium the number of intermediate products, of which polonium (p. 730) is one, is believed to be much greater; this is expressed in the following scheme, in which the simultaneous production of helium (α-rays) is indicated by (α):

Radium (α) → Emanation (α) → Radium A (α) → B → C (α) →
D → E → F (α) →

Radium F is *polonium*, and polonium itself undergoes further change, giving helium and unknown products.

According to Rutherford, a radio-active substance is one which undergoes spontaneous disintegration with liberation of energy. This disintegration cannot be hastened or retarded by any known means; it leads to the production of an unstable substance, which in its turn breaks down into another, and so on, until finally a radio-*in*active and stable element is formed.

Each of these intermediate products disintegrates at a fixed rate, but the rate of change varies enormously with the different substances; thus, whereas it is calculated that the average life of radium is 2500 years, that of radium A (see above) is only about 4 minutes, and that of the emanation about 5 days.

Two 'elements' in addition to uranium, namely, thorium and actinium,* give rise to radio-active substances, and, broadly speaking, the phenomena observed in the case of these elements are analogous to those briefly described in the case of uranium. It may be noted that uranium, and next to it thorium, is the element of highest atomic weight.

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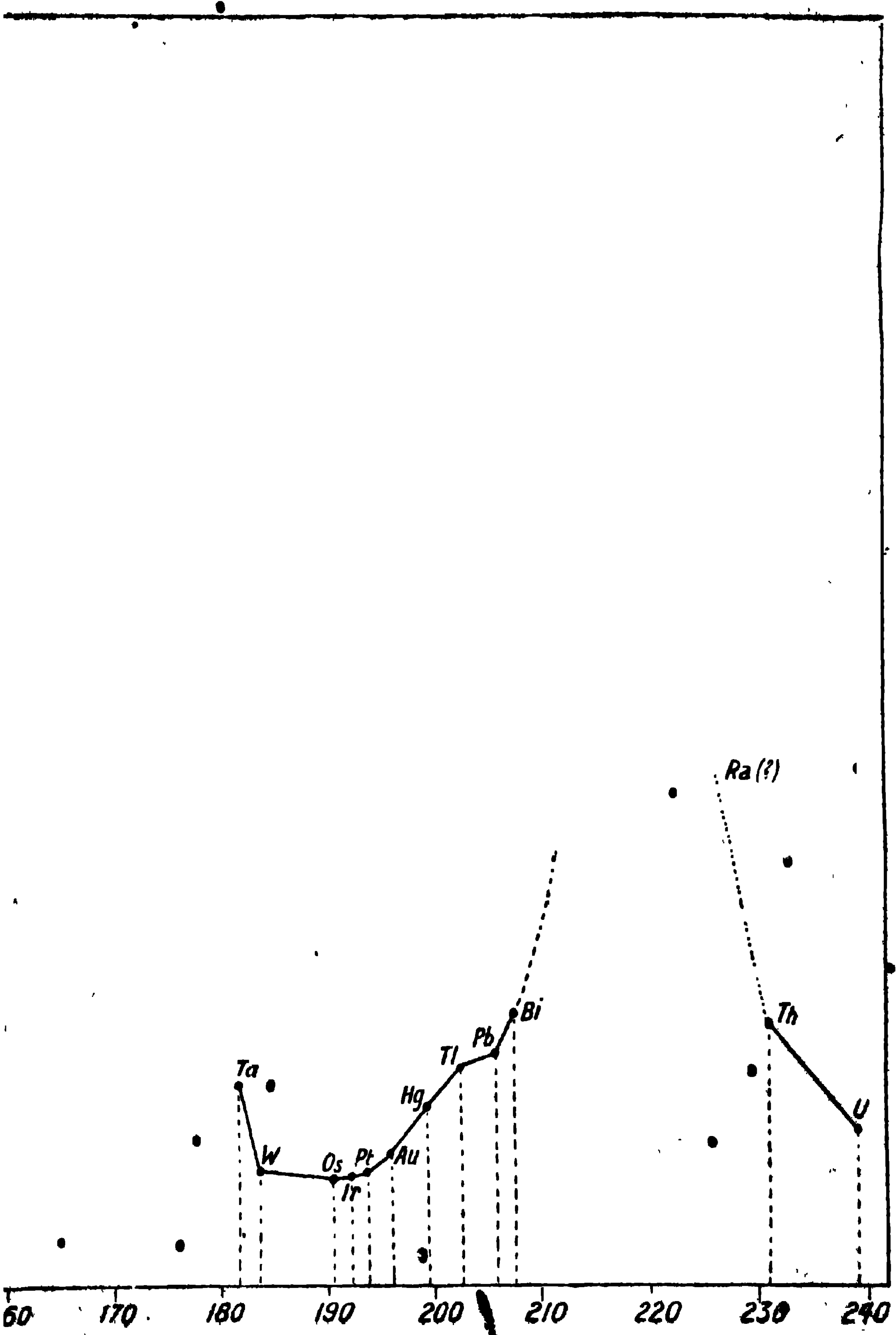
* Found by Debierne in pitch-blende.


Ra (?)
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
60
170
180
190
200
210
220
230
240

RIODIC SYSTEM

B	**C**	**N**	**O**	**F**			SHORT PERIODS
Al	**Si**	**P**	**S**	**Cl**			
Fe	**Ni**	**Co**	**Cu**	**Zn**	**Ga**	**Ge**	
Ru	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	
—	—	—	—	—	—	—	
Os	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	
	VIII		I	II	III	IV	

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[Where more than one reference is given, one being in heavy type, that reference is to the more important description of the subject.]

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		O = 16.			O = 16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·68
Barium	Ba	137·37	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·0
Cæsium	Cs	132·81	Platinum	Pt	195·2
Calcium	Ca	40·09	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·6
Cerium	Ce	140·25	Radium	Ra	226·4
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·1	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·5	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·4	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·62
Gallium	Ga	69·9	Sulphur	S	32·07
Germanium	Ge	72·5	Tantalum	Ta	181·0
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·42
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·85	Tungsten	W	184·0
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·2
Lead	Pb	207·10	Xenon	Xe	128
Lithium	Li	7·00	Ytterbium (Neoytterbium)	Yb	172
Lutecium	Lu	174			
Magnesium	Mg	24·32	Yttrium	Y	89·0
Manganese	Mn	54·93	Zinc	Zn	65·37
Mercury	Hg	200·0	Zirconium	Zr	90·6

The above atomic weights are probably correct to the number of decimal places to which the values are given.